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Treatment Potential for 56 EPA (Environmental Protection Agency) Listed Hazardous Chemicals in Soil

Utah State Univ., Logan

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Robert S. Kerr Environmental Research Lab.
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TREATMENT POTENTIAL FOR 56 EPA LISTED HAZARDOUS CHEMICALS IN SOIL

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16. ABSTRACT

Information is presented for quantitative evaluation of soil treatment potential for 56 hazardous chemicals. The chemicals were organized into four categories: PAH, pesticides, chlorinated hydrocarbons, and miscellaneous chemicals. Treatability studies were conducted to determine: degradation rates, phase partition coefficients, and transformation characteristics. Results of soil fate/transport predictions of two mathematical models were compared with laboratory and literature results to evaluate ability of models to predict behavior of selected chemicals. Experimental approach used was designed to characterize degradation, immobilization, and transformation potentials for the hazardous substances. Results indicated that significance of volatilization and abiotic-loss processes in influencing "apparent loss rates" of substances depended on class of substance. The processes were insignificant for majority of PAHs; biodegradation appears to be major process for PAH loss. Abiotic loss may also be important process for certain pesticides. Volatilization played major role in influencing loss rates of volatiles. Formation of biochemical intermediates was found to be important. Partition coefficients among phases generally indicated a strong affinity for one phase for most substances. Partitioning into soil phase was high for all but most volatile substances. Coefficients calculated using SARs were in good agreement with literature reported values.

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FOREWORD

EPA is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the Laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated and the saturated zones of the surface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on groundwater, soil, and indigenous organics; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

Soil treatment systems that are designed and managed based on a knowledge of soil-waste interactions may represent a significant technology for simultaneous treatment and ultimate disposal of selected hazardous wastes in an environmentally acceptable manner. Decisions pertaining to which wastes and chemicals are amenable to this technology must take into account: 1) the long-term uncertainties associated with the land disposal option; 2) the goal of managing hazardous wastes in an appropriate manner; and 3) the persistence, toxicity, mobility, and propensity to bioaccumulate of hazardous wastes and their hazardous constituents. There is currently a lack of scientifically derived fate and transport information for the wide range of hazardous chemicals for which such decisions can be made. This report presents information pertaining to the quantitative evaluation of the treatment potential in soil for 56 waste constituents identified as hazardous by the United States Environmental Protection Agency (EPA).

Clinton W. Hall

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ABSTRACT

This report presents information pertaining to the quantitative evaluation of the treatment potential in soil for 56 chemicals identified as hazardous by the United States Environmental Protection Agency (EPA). The 56 chemicals evaluated were organized into four categories of substances: (1) polynuclear aromatic hydrocarbons (PAH), (2) pesticides, (3) chlorinated hydrocarbons, and (4) miscellaneous chemicals. Treatability screening studies were conducted to determine: (1) degradation rates, (2) partition coefficients among air, water, soil, and oil phases, and (3) transformation characteristics.

The quantitative information developed for a subset of the tested chemicals was input into two mathematical models (RITZ and VIP) specifically designed to describe the soil treatment process. Results of fate and transport predictions of the models were compared with laboratory and literature results in order to evaluate the ability of the models to predict the behavior of the selected chemicals in a soil system.

The experimental approach used in this study was designed to characterize degradation, immobilization, and transformation potentials for the hazardous substances evaluated. Results indicated that the significance of volatilization and abiotic-loss processes in influencing "apparent loss rates" of substances from soil depends upon the class of substance. These processes were insignificant for the majority of PAH compounds; biodegradation appears to be the major process for the loss of PAH compounds from soil systems. However, abiotic loss may also be an important process for certain pesticide substances. Volatilization was found to play the major role in influencing loss rates of volatile chemicals from soil.

Results from transformation experiments using a radiolabelled chemical indicated that incorporation of the radiolabel into soil organic material was not a significant process in the behavior and fate of the chemical in the soil. The formation of biochemical intermediates was found to be significant. No radiolabelled carbon dioxide was detected in the short-term incubation studies.

Partition coefficients for substances among oil, air, water, and soil phases generally indicated a strong affinity for one phase for most substances. Partitioning into the soil phase was very high for all but the most volatile substances. Partition coefficients calculated using SARs were in good agreement with literature values for coefficients.

Very little leaching or air emissions was predicted by either mathematical model for the subset of pesticides selected, under the simulated test conditions.

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SECTION 1

INTRODUCTION

The Solid and Hazardous Waste Amendments of 1984 (PL 98-616) require the Environmental Protection Agency (EPA) Administrator to promulgate regulations or make determinations regarding whether or not wastes specifically identified or listed under 40 CFR Part 261 shall be prohibited from one or more methods of land disposal, including land treatment. Determinations must be made based on protection of public health and the environment for as long as the waste remains hazardous, taking into account: (1) the long-term uncertainties associated with the land disposal option, (2) the goal of managing hazardous waste in an appropriate manner, and (3) the persistence, toxicity, mobility, and propensity to bioaccumulation of hazardous wastes and their hazardous constituents.

Biodegradation is believed to be the most important degradative mechanism for organic compounds in soil systems and is utilized for transformation of hazardous organic compounds into innocuous products. Biodegradation of organic compounds is accomplished in a series of biochemical reactions through which a parent compound is gradually changed or transformed in soil to organic and inorganic end products. Complete degradation is the term used to describe the process whereby constituents are mineralized to inorganic end products, including carbon dioxide, water, and inorganic species of nitrogen, phosphorus, and sulfur. Aerobic soil bacteria possess the ability to biochemically catalyze the oxidation of compounds using molecular oxygen to initiate reaction sequences, including the Krebs cycle and the fatty acid spiral, that enter central pathways of metabolism (Dagley 1975). In the mixed microbial population of soil systems, one metabolic group of microorganisms may partially metabolize a compound without deriving carbon or energy for cell synthesis through the process of cooxidation, but may furnish a suitable growth substrate for another group. Alternatively, organic compounds may be partially degraded or transformed from parent compounds to organic intermediates that may be recalcitrant and/or toxic.

The primary goal of biodegradation testing is to obtain an overall estimate of the rate at which a compound will biodegrade in a soil environment. General degradation rate models of organics in soils have been described by Hamaker (1972), Goring et al. (1975), Rao and Jessup (1982), U.S. EPA (1984b; 1986a and b), and Hattori and Hattori (1976).

Methods describing the evaluation of biodegradation in natural water and soil media as a means of assessing the persistence of chemical substances in the natural environment (Federal Register, Vol. 44, No. 53, Friday, March 16, 1979, pp. 16272-16280; U.S. EPA 1975), commonly utilize indirect measures, i.e., oxygen consumption, CO_2 evolution, and dissolved organic carbon (DOC) loss, to assess the persistence of compounds in test environments and to predict the relative importance of biodegradation as a factor affecting compound persistence. While these procedures provide a qualitative assessment of biodegradation, results do not provide a means of determining quantitative rates of degradation for specific constituents that are essential for the assessment of compound fate and transport as well as for risk analysis (Federal Register 1979). For quantitative assessment of the rate of biodegradation of an individual constituent in a soil system, it is necessary to measure (1) changes in parent compound concentration with time, (2) loss of chemical due to volatilization, and (3) chemical loss due to abiotic mechanisms.

In addition to the degradation of hazardous constituents, the immobilization potential (partitioning into soils, liquid, and gaseous phases) and the transformation of parent compounds to intermediate products within a soil system represent additional information requirements for assessing soil treatment potential for hazardous constituents.

The information generated in this study concerning degradation, transformation, and immobilization was entered into a comprehensive soil fate and transport data base developed as part of a concurrent EPA-funded study. Specific quantitative information concerning persistence and/or partitioning (mobility) for 56 specific substances was developed to provide EPA with treatability information for making decisions concerning the management of land disposal sites. The 56 substances were organized into four classes for evaluation: polynuclear aromatic hydrocarbons (PAHs), pesticides, chlorinated hydrocarbons and miscellaneous compounds.

The information was also intended for use in mathematical models developed to evaluate the treatment potential for specific substances in soil. Use of such models provides an approach for integration of the simultaneous processes of degradation and partitioning in soil systems so that an assessment can be made of the presence of hazardous substances in leachate, soil, and air. Models provide an estimate of the potential for groundwater and air contamination through a determination of the rate and extent of contaminant transport and degradation for particular site/ soil/compound characteristics. Description of quantitative organic chemical decomposition and mobility in soil systems also allows the identification of chemicals or classes of chemicals that require management through control of mass transport and/or treatment to reduce or eliminate their hazard potential (U.S. EPA 1984b, Mahmood and Sims 1986).

The two models used in this study to evaluate fate and transport behavior in soil systems were: (1) the Regulatory and Investigative Treatment Zone (RITZ) Model and (2) the Vadose Zone Interactive Processes (VIP) Model. The RITZ Model was developed at the Robert S. Kerr Environmental Research Laboratory (RSKERL), Ada, Oklahoma (Short 1986); the VIP Model which uses RITZ as its base was developed at Utah State University under a cooperative project with the RSKERL (Grenney et al. 1987).

Transformation studies were performed with the McLaurin sandy loam soil at low pH and the same soil adjusted to neutral pH for 7,12-dimethylbenzanthracene (DMBA). Soil pH was adjusted from 4.8 to 7.5 by adding 70 mg of $CaCO_3$ to the McLaurin soil. DMBA was chosen based on reported genetic toxicity (Shoza et al. 1974, Walters 1966) and the rate and extent of degradation measured in laboratory studies (Park 1987).

OBJECTIVES

The overall objective of this research project was to provide soil treatability information for 56 specific chemicals identified as hazardous by EPA. The emphasis was placed on the development of degradation rates and transport information in the form of partition coefficients that could be used as input to mathematical models for evaluation of pollutant behavior in soil systems.

Specific objectives of the research project were to:

(1) Determine biodegradation rates corrected for volatilization.

(2) Determine the extent of soil incorporation into soil organic material and the biological and chemical characterization of transformation products.

(3) Determine the contribution of abiotic loss to "apparent loss rates."

(4) Calculate partition coefficients among oil, water, air, and soil phases.

(5) Input the degradation rate and partition coefficient data into the RITZ and VIP fate and transport Models.

APPROACH

Degradation kinetic information and/or transport data were developed for 56 substances identified by EPA as requiring quantitative evaluation for soil treatment potential. Laboratory experiments were conducted using two agricultural soils to generate degradation rates corrected for volatilization and for abiotic loss for a subset of substances and apparent loss rates for another subset of substances.

Biodegradation rates were determined experimentally by applying the chemical of interest to a soil microcosm and monitoring concentration over time. A plot of the disappearance of a constituent originally present in the substance/soil mixture versus treatment time can provide the following information:

1) The reaction order of the process (generally zero or first order),

2) The reaction rate constant, K (mass constituent/mass soil-time for zero order reactions or 1/time for first order reactions), and

3) The half-life ($t_{1/2}$, time) of each constituent of concern.

Methods were employed for the determination of biodegradation rates corrected for volatilization losses when necessary and for losses in microbial inactive soil/substance controls that indicate contribution to degradation of abiotic (e.g., hydrolysis, oxidation, etc.) processes. Incubation in the absence of light was used for all substances to prevent compound decomposition due to photodegradation.

Biodegradation information, which is normally reported as half-life in soil, can be used to evaluate:

a) Effect of biodegradation on the attenuation of constituent transport through a soil profile,

b) Effect of soil and constituent characteristics on constituent biodegradation and constituent transport through the soil profile, and

c) Effect of environmental parameters, including pH, dissolved oxygen, nutrients, and amendments on biodegradation of test substances.

Transformation was evaluated using radiolabelled 7,12-dimethylbenz(a)anthracene (DMBA). A mass balance for DMBA among soil, gaseous, and solvent extractable fractions over incubation time was evaluated to determine the extent of incorporation of the chemical into the soil matrix. Chemical and toxicologial properties of biochemical intermediate products were also characterized. The distribution of radiolabelled material between parent compounds and biochemical intermediates was also characterized.

Transport data were developed using calculational procedures based on structure-activity relationships (SARs). Partition coefficients among soil, air, oil, and water phases were determined for each substance.

Degradation kinetic information and partition coefficients among soil, oil, aqueous, and gaseous phases developed in this project were entered into the comprehensive data base compiled for EPA concerning the fate and behavior of hazardous substances in soil systems (Soil Transport and Fate Date Base).

SECTION 2

CONCLUSIONS

Specific conclusions based on the objectives of this research project include:

(1) The importance of volatilization and abiotic-loss processes in influencing "apparent loss rates" of substances from soil systems depends upon the class of substances. These processes are insignificant for the majority of PAH compounds. Biodegradation appears to be the major process for the loss of PAHs from soil systems. Abiotic loss may be an important process for certain pesticide substances. Volatilization appears to be the major process influencing loss rates of volatile substances from soil systems.

(2) Transformation products of mutagenic parent substances may exhibit mutagenic characteristics, but may decrease in mutagenic potential with incubation time in soil. A decrease in the concentration of parent substance in a soil extract solution that is not accompanied by an increase in carbon dioxide evolution may not indicate irreversible soil incorporation of applied waste. Rather, intermediate biochemical transformation products may occur that exhibit changing characteristics with time of incubation in the soil.

(3) Mercuric chloride is effective for reducing soil bacteria and fungi to levels at least as low as 10 organisms per gram of soil (dry-weight basis). However, the use of $HgCl_2$ may greatly affect the recovery of certain compounds from soil. The use of $HgCl_2$ sterile controls for biodegradation studies should be further examined.

(4) It is possible to develop transport information for mathematical models as partition coefficients based on structure-activity relationships (SARs) for substances that are difficult to evaluate experimentally.

(5) In laboratory experiments using the U.S. EPA treatment models, under environmental and loading rate conditions representative of well designed and managed land treatment systems, very little transport of either pesticides or PAH compounds was predicted, including leaching and air emissions. The same conclusions were found in the literature citations used in this study.

SECTION 3

RECOMMENDATIONS

Based on the methodology used; experimental design; data handling; degradation, transformation, and partitioning information developed; and mathematical modeling concerning the treatability of hazardous substances in soil systems, the following recommendations are made:

(1) Techniques to manage volatile chemicals to accomplish in situ treatment should be developed and evaluated for wastes containing volatile substances.

(2) Transformation products of parent hazardous substances should be evaluated for potential toxicity and mutagenicity. Also, the fate and behavior (degradation, detoxification, and partitioning) of transformation products should be evaluated in greater detail for all hazardous substances investigated.

(3) Additional research is required for evaluation of the ability of soil treatment mathematical models to predict the transport of hazardous substances under field conditions. A subset of hazardous substances within each class of waste constituents should be evaluated using the models at full-scale sites.

(4) Techniques should be evaluated to address the problem of quantification and characterization of biotic and abiotic degradation mechanisms in soil systems for chlorinated and organophosphorus pesticides.

SECTION 4

METHODS AND PROCEDURES

DESIGNATED CHEMICALS AND WASTE

Tables 1 through 4 list 56 substances identified by the EPA Project Officer for evaluation of degradation and immobilization information. Four categories of substances were evaluated including polynuclear aromatic hydrocarbons (PAHs), pesticides, chlorinated hydrocarbons, and miscellaneous substances. Tables 1 through 4 also contain characterization information for each substance including chemical formula, chemical abstract service (CAS) number, and EPA hazardous waste number, as well as physical-chemical property information for each substance including melting point, boiling point, vapor pressure, and aqueous solubility. The physical-chemical information was used in calculational procedures, based on structure-activity relationships (SARs), to calculate partition coefficients among oil, soil, aqueous, and air phases of a soil system.

All chemicals except toxaphene and tetraalkylead (TAL) were purchased commercially, analytical grade. The toxaphene sample was collected from a site where spent toxaphene dipping solution, used in cattle operations, had been disposed of on soil. The waste sample consisted of soil, manure, cattle hair, and partially degraded toxaphene. The TAL sample was provided by Standard Oil and consisted of tetraalkyllead (61.5%), ethylene dibromide (17.9%), and ethylene dichloride (18.8%).

TABLE 1. CHARACTERIZATION INFORMATION AND SELECTED PROPERTIES FOR 16 PAH COMPOUNDS.

Compound	Formula	EPA Code	CAS No.	MW	MP (°C)	Ref	BP (C)	Ref
Acenaphthylene	C12H10	X011	208-96-8	152.2	92	Sims and Overcash, 1983	279	Sims and Overcash, 1983
Benz(a)anthracene	C18H12	U018	56-55-3	228	158	Sims and Overcash, 1983	400	Sims and Overcash, 1983
Benzo(a)pyrene	C20H12	U022	50-32-8	252.3	179	Sims and Overcash, 1983	496	Sims and Overcash, 1983
Chrysene	C8H12	U050	218-01-9	228.2	254	Sims and Overcash, 1983	448	Verschueren, 1977
Dibenzo(a,h)anthracene	C22H14	U063	53-70-3	278.36	270	U.S. EPA, 1983	-	-
Indeno(1,2,3-cd)pyrene	C22H12	U137	193-39-5	276.34	163	Sims and Overcash, 1983	-	-
3-Methylcholanthrene	C21H16	U157	56-49-5	268.3	180	U.S. EPA, 1983	280	U.S. EPA, 1983(70 torr)
Fluoranthene	C16H10	U120	206-44-0	202	111	Sims and Overcash, 1983	250	Verschueren, 1977
1-methylnaphthalene	C11H10	-	90-12-0	142.2	-22	Verschueren, 1977	245	Sims, 1986
Naphthalene	C10H8	U165	91-20-3	128.16	80.2	Sims and Overcash, 1983	217.9	Sims and Overcash, 1983
Phenanthrene	C14H10	-	85-01-8	178.22	101	Sims and Overcash, 1983	340	Sims and Overcash, 1983
Pyrene	C16H10	-	129-00-0	202.24	149	Sims and Overcash, 1983	360	Sims and Overcash, 1983
Benzo(b)fluoranthene	C20H12	-	205-99-2	252	167	Sims and Overcash, 1983	-	-
7,12-dimethylbenzanthracene	C20H16	U094	57-97-6	256.3	122.5	U.S. EPA, 1984	-	-
anthracene	C14H10	-	120-12-7	178.22	216	Sims and Overcash, 1983	340	Sims and Overcash, 1983
Benz(c)acridine	C17H11N	U016	225-51-4	229.3	-	-	-	-

TABLE 1. CONTINUED

Compound	V.P. (mmHg)	Ref	Aqueous (mg/L)	Aqueous sol (M)	Ref	log Kow	Ref	log Koc*
Acenaphthylene	2.90E-02	Sims and Overcash, 1983(20°C)	3.93	2.58E-05	Sims and Overcash, 1983	4.07	Sims and Overcash, 1983	3.68
Benz(a)anthracene	5.00E-09	Sims and Overcash, 1983(20°C)	1.40E-02	6.14E-08	Sims and Overcash, 1983	5.61	Sims and Overcash, 1983	5.20
Benzo(a)pyrene	5.00E-07	Sims and Overcash, 1983(20°C)	3.80E-03	1.51E-08	Sims and Overcash, 1983	6.04	Sims and Overcash, 1983	5.63
Chrysene	6.30E-07	Sims and Overcash, 1983(20°C)	2.00E-03	8.76E-09	Sims and Overcash, 1983	5.61	Sims and Overcash, 1983	5.20
Dibenzo(a,h)anthracene	1.00E-10	U.S EPA, 1983 (20°C)	5.00E-04	1.80E-09	U.S EPA,1983	5.97	U.S. EPA, 1983	5.56
Indeno(1,2,3-cd)pyrene	1.00E-10	Sims and Overcash, 1983(20°C)	6.20E-02	2.24E-07	Sims and Overcash, 1983	7.66	Sims and Overcash, 1983	7.23
3-Methylcholanthrene		-	1.10E-08	4.10E-14	Mackay and Shiu, 1977	7.11	calculated	6.69
Fluoranthene	6.00E-06	Sims and Overcash, 1983(20°C)	2.60E-01	1.29E-06	Sims and Overcash, 1983	5.33	Sims and Overcash, 1983	4.93
1-methylnaphthalene	1.31E-06	calculated	2.85E+01	2.00E-04	Mackay and Shiu, 1977	3.87	Miller et al., 1985	3.48
Naphthalene	4.92E-02	Sims and Overcash, 1983(20°C)	3.17E+01	2.47E-04	Sims and Overcash, 1983	3.35	Miller et al., 1985	2.97
Phenanthrene	6.80E-04	Sims and Overcash, 1983(20°C)	1.30E+00	7.28E-06	Sims and Overcash, 1983	4.46	Sims and Overcash, 1983	4.06
Pyrene	6.85E-07	Sims and Overcash, 1983(20°C)	1.40E-01	5.92E-07	Sims and Overcash, 1983	5.32	Sims and Overcash, 1983	4.92
Benzo(b)fluoranthene	5.00E-07	Sims and Overcash, 1983(20°C)	5.50E-03	2.18E-08	Sims and Overcash, 1983	6.57	Sims and Overcash, 1983	6.15
7,12-dimethylbenzanthracene	-	-	2.40E-02	9.36E-08	U.S. EPA, 1984	5.98	U.S. EPA, 1984	5.57
anthracene	1.96E-04	Sims and Overcash, 1983(20°C)	7.30E-02	4.10E-07	Sims and Overcash, 1983	4.45	Sims and Overcash, 1983	4.06
Benz(c)acridine	-	-	-	-	-	-	-	-

*calculated from regression equation developed by Karickhoff et al. (1979).

TABLE 2. CHARACTERIZATION INFORMATION AND SELECTED PHYSICAL PROPERTIES FOR 22 PESTICIDES.

Compound	Formula	EPA Code	CAS No.	MW	MP (°C)	Ref	BP (°C)	Ref
Aldrin (1)	C12H8CL6	P004	30900-2	364.9	107	U.S EPA, 1983		
Cacodylic Acid	C2H7As02	U136	75-60-5	137.99	195	U.S EPA, 1983		
Chlordane, technical (1)	C10H6Cl8	U036	57-74-9	409.8	107	U.S EPA, 1983	175	U.S EPA, 1983
DDT (1)	(ClC6H4)2CCCl2	U061	50-29-3	354.5	108	Verschuenen, 1977	185	U.S EPA, 1983
Dieldrin (1)	C12H8OCl6	P037	60-57-1	380.93	175	MSDS†	-	-
Dinoseb	C10H12N2O5	P020	88-85-7	240.22	40	MSDS	-	-
Disulfoton (2)	C8H19O2PS3	P039	298-04-4	274.4	-	-	62	MSDS
Endosulfan (1)	C9H6CL6O3S	P050	115-29-7	406.95	106	MSDS	-	-
Famphur	C10H16NO5PS2	P097	52-85-7	325	53	MSDS	-	-
Heptachlor (1)	C10H5CL7	P059	76-44-8	373	95	MSDS	-	-
Lindane (alpha) (1)	C6H6Cl6	U129	319-84-6	290.85	157	Verschuenen, 1977	288(decomp)	Verschuenen, 1977
Methyl parathion (2)	C6H10O5NPS	P071	298-00-0	263.2	35-36	U.S EPA, 1983	-	-
Parathion (2)	C10H14O5NPS	P089	56-38-2	291.3	6	MSDS	375	Merck Index, 1968
Phorate (2)	C7H17O2PS3	P094	298-02-2	260	<-15	U.S EPA, 1983	118-120	U.S EPA, 1983 (0.8 torr)
Pronamide	C12H11Cl2NO	U192	23950-58-5	255.9	155-156	MSDS	-	-
Toxaphene (1)	C10H10Cl8	P123	8001-35-2	413	85	Cohen et al., 1982	>120 (Decomp)	Cohen et al., 1982
Warfarin	C19H16O4	P001	81-81-2	308	161	MSDS	-	-
Aldicarb	C7H14N2O2S	P070	116-06-3	190.25	99-100	MSDS	-	-
pentachloronitrobenzene	C6Cl5NO2	U185	82-68-8	295.34	141.5	Verschueren, 1977	328	MSDS
Diethyl-p-nitrophenyl phosphate (2)	C10H14O6NP	P041	311-45-5	275.21	-	-	169	Merck Index, 1968
Floracetic acid	FCH2CO2Na	P028	62-74-80	100.02	33	U.S. EPA, 1983	165	U.S. EPA, 1983
Formaldehyde	HCHO	U122	50-00-0	30.03	-118	Verschueren, 1977	-19.4	U.S. EPA, 1983

† MSDS = Materials Safety Data Sheet

(1) = Chlorinated Hydrocarbon
(2) = Organophosphate

TABLE 2. CONTINUED

Compound	V.P. (mmHg)	Ref	Aqueous Sol (mg/L)	Aqueous Sol (M)	Ref	log Kow	Ref	log Koc*
Aldrin (1)	6.00E-06	Edwards, 1972 (20-25°C)	0.01	2.74E-08	Wauchope, 1978	0.85	Felsot and Dahm, 1979	2.61
Cacodylic Acid			6.67E+01	4.83E-04	U.S. EPA, 1983	0.00	U.S. EPA, 1983	-0.35
Chlordane, technical (1)	1.00E-05	Edwards, 1972 (20 °C)	5.60E-02	1.37E-07	U.S. EPA, 1983 (20°C)	2.78	U.S. EPA, 1983	2.40
DDT (1)	1.90E-07	Edwards, 1972 (20-25°C)	1.00E-03	2.82E-09	Edwards, 1972	3.48	U.S. EPA, 1983	3.10
Dieldrin (1)	1.00E-07	Edwards, 1972 (20-25°C)	1.00E-01	2.63E-07	Wauchope, 1978	2.90	U.S. EPA, 1983	2.52
Dinoseb	>1.00E-06	Weber, 1972 (20-25 C)	5.20E+01	Weber, 1972		2.30	Rao and Davidson, 1980	2.30
Disulfoton (2)	3.00E-04	U.S. EPA, 1984 (20-25 °C)	6.00E+01	2.19E-04	U.S. EPA, 1984	0.00	U.S. EPA, 1983	3.25
Endosulfan (1)	1.00E-05	Goebel et al., 1982	6.00E-02	1.47E-07	U.S. EPA, 1983	3.55	U.S. EPA, 1983	3.16
Famphur	-	-	-	-	-	-	-	-
Heptachlor (1)	3.00E-04	Edwards, 1972 (20 °C)	5.60E-02	1.50E-07	U.S. EPA, 1983	3.90	U.S. EPA, 1983	3.51
alpha Lindane (1)	2.15E-05	U.S. EPA, 1983 (20°C)	1.00E+01	3.44E-05	Verschueren, 1977	3.81	U.S. EPA, 1983	3.42
Methyl parathion (2)	9.70E-06	U.S. EPA, 1983	5.00E+01	1.90E-04	U.S. EPA, 1983	2.99	Hansch and Leo,1979	2.61
Parathion (2)	3.78E-05	U.S. EPA, 1983	6.54E+00	2.25E-05	Felsot and Dahm, 1979	3.40	Felsot and Dahm, 1979	3.02
Phorate (2)	2.30E-03	U.S EPA, 1984	8.00E+01	3.08E-04	Wauchope, 1978	2.92	Holden, 1986	2.54
Pronamide	8.00E-02	U.S. EPA, 1983 (20°C)	1.50E+01	5.86E-05	Merck Index, 1968	-	-	2.30
Toxaphene (1)	1.00E-06	Cohen et al., 1982	3.00E+00	7.26E-06	Edwards, 1972	3.30	Cohen et al., 1982	2.92
Warfarin		-	-	-	-	2.52	Hansch and Leo,1979	2.15
Aldicarb	1.00E-04	Holden, 1986	4000	2.10E-02	Felsot and Dahm, 1979	0.70	Holden, 1986	0.35
Pentachloronitrobenzene	1.01E-10	calculated	0.44	1.49E-06	U.S EPA. 1983	5.57	U. S. EPA. 1983	-
Diethyl-p-nitrophenyl phosphate (2)		-	-	-	-	-	-	-
Fluoracetic acid, sodium salt	-	-	-	-	-	-	-	-
Formaldehyde	10	Verschueren, 1977 (-88 C)	-	-	-	-	-	-

*calculated from regression equation developed by Karickhoff et al. (1979).

(1) = Chlorinated Hydrocarbon
(2) = Organophosphate

TABLE 3. CHARACTERIZATION INFORMATION AND SELECTED PHYSICAL PROPERTIES FOR 13 CHLORINATED HYDROCARBONS.

Compound	Formula	EPA Code	CAS No.	MW	MP (°C)	Ref	BP (C)	Ref
Bis-(chloromethyl) ether	CH2ClOCH2Cl	P016	542-88-1	114.96	-41.5	Verschueren, 1977	104	Verschueren, 1977
Chloromethyl methyl ether	ClCH2OCH3	U046	107-30-2	80.52	-103.5	Verschueren, 1977	59.5	Verschueren, 1977
1,2-Dibromo-3-chloropropane	C3H5ClBr2	U066	46-12-8	236.4			196	Merck Index, 1968
Dichlorodifluoromethane	CCl2F2	U075	75-71-8	120.91	-158	Verschueren, 1977	-29.8	Verschueren, 1977
1,1-Dichloroethylene	C2H2Cl2	U078	75-35-4	96.94	-122	Verschueren, 1977	31	Aldrich, 1986
1,1,1-Trichloroethane	CCl3CH3	U226	71-55-6	133.41	-32	Verschueren, 1977	74-76	Aldrich, 1986
1,1,2,2-Tetrachloroethane	CH2ClCCl3	U209	79-34-5	167.9	-36	Verschueren, 1977	146.2	Verschueren, 1977
1,1,2-Trichloroethane	CH2ClCHCl2	U227	79-00-5	133.41	-35	Aldrich, 1986	113.7	Verschueren, 1977
1,1,2-Trichlorotrifluoroethane	CFCl2CF2Cl	X001	76-13-1	187.38	-35	Aldrich, 1986	47	Aldrich, 1986
Trichloromonofluoroethane	C2H2Cl3F	U121	75-69-4	137.38	-111	U.S. EPA, 1983	24.1	U.S. EPA, 1983
Hexachlorocycopentadiene	C5Cl6	U130	77-47-7	272.77	9	U.S. EPA, 1983	239	U.S. EPA, 1983
4,4-Methylene-bis-(2-chloroaniline)	CH2(C6H4ClNH2)2	U158	101-14-4	267.2	-85.9	U.S. EPA, 1983	79.6	U.S. EPA, 1983
1,2,4-trichlorobenzene	C6H3Cl3	X105	120-82-1	181.46	17	Verschueren, 1977	214	Aldrich, 1986

Compound	V.P. (mmHg)	Ref	Aqueous Sol (mg/L)	Aqueous Sol (M)	Ref	log Kow	Ref	log Koc*
Bis-(chloromethyl) ether	3.00E+01	U.S. EPA, 1983 (22 C)	2.20E+04	1.91E-01	U.S. EPA, 1983 (20°C)	-0.38	U.S. EPA, 1983	-0.72
Chloromethyl methyl ether	2.04E+00	calculated				0.91	U.S. EPA, 1983	0.55
1,2-Dibromo-3-chloropropane	8.00E+00	Merck Index, 1968						
Dichlorodifluoromethane	4.36E+03	U.S. EPA, 1983 (20°C)	2.80E+02	2.32E-03	U.S. EPA, 1983	2.16	U.S. EPA, 1983	1.79
1,1-Dichloroethylene	5.00E+02	Verschueren, 1977 (20°C)						
1,1,1-Trichloroethane	1.00E+02	Verschueren, 1977 (20°C)	4.40E+03	3.30E-02	Verschueren, 1977 (20°C)	2.2	U.S. EPA, 1983	1.83
1,1,2,2-Tetrachloroethane	5.00E+00	U.S. EPA, 1983 (20°C)	2.90E+03	1.73E-02	U.S. EPA, 1983	4.99	U.S. EPA, 1983	4.59
1,1,2-Trichloroethane	1.90E+01	U.S. EPA, 1983 (20°C)	4.40E+03	3.30E-02	Merck Index, 1968	2.17	U.S. EPA, 1983	1.80
1,1,2-Trichlorotrifluoroethane	2.70E+02	Verschueren, 1977 (20°C)				1.66	calc	1.30
Trichloromonofluoroethane	2.36E+01	calculated						
Hexachlorocycopentadiene	8.00E-02	U.S EPA, 1983 (25 C)	2.73E+01	1.00E-04	U.S. EPA, 1983	5.04	McDuffie, 1981	4.64
4,4-Methylene-bis-(2-chloroaniline)	3.69E-01	calculated				3.3	Holden, 1986	2.92
1,2,4-trichlorobenzene	4.46E-06	calculated	2.54E-04	1.40E-09		3.98	Miller et al.,1985	3.59

*calculated from regression equation developed by Karickhoff et al. (1979).

TABLE 4. CHARACTERIZATION INFORMATION AND SELECTED PHYSICAL PROPERTIES FOR 5 MISCELLANEOUS COMPOUNDS.

Compound	Formula	EPA Code	CAS No.	MW	MP (°C)	Ref	BP (C)	Ref
Aniline	C6H5NH2	U012	62-53-3	93.1	-6	Verschueren, 1977	184	Verschueren, 1977
Mitomycin C	C15H18N4O5	U010	50-07-7	334.34	360	Merck Index, 1968	-	-
Pyridine	'CHCHCHCHCHN'	U196	110-86-1	79.1	-42	Verschueren, 1977	115.2	Verschueren, 1977
Tetraethyl Lead	PB(C2H5)4	P110	78-00-2	323.44	-136	Verschueren, 1977	110-200(D)	Verschueren, 1977
Uracil mustard	C8H11Cl2N3O2	U237	66-75-1	252.1	206	Merck Index, 1968	-	-

Compound	V.P. (mmHg)	Ref	Aqueous Sol (mg/L)	Aqueous sol (M)	Ref	log Kow	Ref	log Koc*
Aniline (amino benzene)	3.00E-01	Verschueren, 1977	3.40E+04	3.65E-01	Verschueren, 1977	0.96	U.S. EPA, 1983	0.60
Mitomycin C	-	-	-	-	-	-0.038	Hansch,1979	-0.38
Pyridine	1.40E+01	U.S. EPA, 1983 (20°C)	-	-		0.66	U.S. EPA, 1983	0.31
Tetraethyl Lead	1.50E-01	Verschueren, 1977 (20°C)	2.91E-01	9.00E-07	-	-	-	-
Uracil mustard	-	-	-	-	-	-1.07	Hansch and Leo, 1979	-1.40

*calculated from regression equation developed by Karickhoff et al. (1979).

SOIL CHARACTERIZATION

Two soils used in this study were a Kidman fine sandy loam (Haplustoll, Utah) and a McLaurin sandy loam soil (Paleudult, Mississippi). Surface soil to a depth of approximately 6 inches was sampled for each soil type. The collected soils were air-dried and sieved to pass a 2-mm sieve. Physical and chemical properties of the soils are shown in Tables 5 and 6. These soils had not received application of any fertilizer or agricultural chemical in the last five years. Soil microorganism counts (Tables 5 and 6) are typical for a soil with an active microbial populations.

DETERMINATION OF DEGRADATION RATES IN SOIL

Degradation describes the chemical and/or biological conversion of a parent compound to its various intermediates (transformation) and/or to inorganic end products such as carbon dioxide, water, nitrogen, phosphorous, sulfur, etc. (complete degradation). In this study, the rate of degradation was experimentally determined by measuring the difference between the amount of compound initially added to a soil and that which was recovered after specified time intervals. Using sterile soil control samples rendered microbially inactive using $HgCl_2$ (Fowlie and Bulman 1986), the biological and chemical degradation components were differentiated. This operational determination of degradation, however, could not be used to distinguish between complete degradation and transformation into intermediate products. Transformation was characterized for one chemical, 7,12-dimethylbenzanthracene (DMBA).

TABLE 5. CHARACTERIZATION OF KIDMAN SANDY LOAM SOIL COLLECTED FROM USU AGRICULTURAL EXPERIMENT FARM AT KAYSVILLE, UTAH

Soil Characteristic	Value
Physical Properties:	
Bulk density*	1.49 g/cm^3
Texture*	loam
Moisture at	
1/3 atmosphere	20%
15 atmospheres	7%
Saturation*	24%
Soil Classification:	Typic Haplustoll
Chemical Properties:	
pH	7.9
CEC	10.1 meq/100g
Organic carbon*	0.5%
Total phosphorus	0.06%
Total nitrogen	0.07%
Nitrate nitrogen	3.7 ppm
Sulfate in saturated extract	4.8 ppm
EC of saturated extract	0.2 mmhos/cm
Iron	9.0 ppm
Zinc	1.2 ppm
Phosphorus (bicarbonate extractable)	27 ppm
Potassium	117 ppm
Ammonium acetate-extractable cations	
Sodium	0.24 meq/100g
Potassium	0.42 meq/100g
Calcium	13.6 meq/100g
Magnesium	1.7 meq/100g
Water soluble cations	
Sodium	0.01 meq/100g
Potassium	<0.01 meq/100g
Calcium	0.04 meq/100g
Magnesium	0.01 meq/100g
Biological Properties:	
Soil plate counts	
Bacteria	6.7 x 10^6/g
Fungi	1.9 x 10^4/g

*Soil properties required for use in modeling soil treatment of hazardous waste (U.S. EPA 1986b).

TABLE 6. CHARACTERIZATION OF MCLAURIN SANDY LOAM SOIL PROVIDED BY MISSISSIPPI STATE UNIVERSITY, WIGGINS, MS

Soil Characteristic	Value
Physical Properties:	
Bulk density*	1.41 g/cm^3
Texture*	Sandy loam
Moisture at	
1/3 atmosphere	12.4%
15 atmospheres	8.2%
Saturation*	20%
Soil Classification:	Typic Paleudults
Chemical Properties:	
pH	4.8
CEC	6.35 meq/100g
Organic carbon*	0.94%
Total phosphorus	0.003%
Total nitrogen	0.02%
Nitrate nitrogen	0.08 ppm
Sulfate in saturated extract	13.7 ppm
EC of saturated extract	0.25 mmhos/cm
Iron	18 ppm
Zinc	0.64 ppm
Phosphorus (bicarbonate extractable)	2.2 ppm
Potassium	19 ppm
Ammonium acetate-extractable cations	
Sodium	0.02 meq/100g
Potassium	0.07 meq/100g
Calcium	0.29 meq/100g
Magnesium	0.06 meq/100g
Aluminum	1.45 meq/100g
Hydrogen	5.91 meq/100g
Water soluble cations	
Sodium	0.100 meq/100g
Potassium	0.003 meq/100g
Calcium	0.270 meq/100g
Magnesium	0.088 meq/100g
Biological Properties:	
Soil plate counts	
Bacteria	6.3 x 10^5/g
Fungi	7.5 x 10^4/g

*Soil properties required for use in modeling soil treatment of hazardous waste (U.S. EPA 1986b).

Two experimental approaches were used to measure degradation rates for the chemicals evaluated in the study. In the first approach degradation rates were not corrected for volatilization losses (Table 7). That is the observed loss of a compound due to volatilization was not distinguished from losses attributed to degradation. In the second approach, degradation rates were corrected for volatilization (Table 8). The later approach provided independent measurement of losses due to volatilization thus allowing a corrected degradation rate to be determined.

Determination of Degradation Rates (Uncorrected for Volatilization)

Soil microcosms consisted of 250 mL glass beakers containing 50 g of either Kidman or McLaurin soil. Each soil sample was initially wetted to achieve a moisture content of -0.3 bar matric potential. The soils were then incubated at 20°C for a minimum of five hours.

Chemicals were then applied to the incubated soils in 2 to 5 mL of n-hexane, methanol, or methylene chloride either as individual constituents or in mixtures. Loading rates are given in Tables 7 and 8. Samples were thoroughly mixed and the solvent was allowed to evaporate. The beakers were then covered with a polyethylene sheet. This material, which is permeable to air but impermeable to water, was used to minimize water loss. All soil/chemical mixtures were incubated at 20°C in the dark to prevent photodegradation of the chemicals tested. Samples were periodically weighted and deionized water was added to maintain soils at -0.3 bar matric potential.

Triplicate samples were removed from incubation for extraction and parent compound quantitation at various time intervals, based on an estimated half-life of the chemical. The soils were extracted directly in

TABLE 7. LOADING RATES FOR SELECTED COMPOUNDS ON KIDMAN AND MCLAURIN SOILS FOR WHICH DEGRADATION RATES WERE UNCORRECTED FOR VOLATILIZATION

Compound	Loading Rate (mg/kg)	Chemical Matrix	
		Individual Constituent	Synthetic Mixture
Polynuclear Aromatic Hydrocarbons			
Anthracene	200	X	
Phenanthrene	900	X	
Fluoranthene	900	X	
Pyrene	700	X	
Chrysene	100	X	
Benz(a)anthracene	100	X	
7,12 Dimethylbenz(a)-anthracene	16	X	
Benzo(b)fluoranthene	38	X	
Dibenz(a,h)anthracene	12.5	X	
Benzo(a)pyrene	33	X	
Dibenzo(a,i)pyrene	10	X	
Indeno(1,2,3-cd)pyrene	9.0	X	
Acenaphthylene	96.99		A[1]
3-Methylcholanthrene	32.25		A
Pesticides			
Aldrin	0.45	X	
Heptachlor	0.67	X	
Endosulfan	0.69	X	
Disulfoton	1.58	X	
Phorate	1.64	X	
Parathion	1.83	X	
Methylparathion	1.60	X	
Dichlorodiphenyl-trichloroethane	0.50		B
Pentachloronitrobenzene	0.34		B
Lindane	0.49		C
Aldicarb	99		D
Famphur	99		D
Warfarin	98		D
Dinoseb	102.88		A
Pronamide	99.33		A
Toxaphene	20	2	
Chlorinated Hydrocarbons			
1,2,4 trichlorobenzene	0.732		B
Hexachlorocyclopentadiene	0.340		C
Miscellaneous			
Aniline	100		D

[1] letters indicate compounds included in given mixture.

[2] Toxaphene was evaluated as an individual constituent within a complex waste consisting of soil, manure, cattle hair, and partially degraded dexaphene used in a cattle dipping solution.

TABLE 8. LOADING RATES FOR SELECTED COMPOUNDS ON KIDMAN AND MCLAURIN SOILS FOR WHICH DEGRADATION RATES WERE CORRECTED FOR VOLATILIZATION.

Compound Synthetic	Loading Rate (mg/kg)	Chemical Matrix Individual Constituent	 Mixture
Polynuclear Aromatic Hydrocarbons			
Naphthalene	100	X	
1-Methylnaphthlene	100	X	
Anthracene	200	X	
Phenantherene	900	X	
Fluoranthene	900	X	
Pyrene	690	X	
Chrysene	100	X	
Benz(a)anthracene	100	X	
7,12 Dimethylbenz(a)anthracene	16	X	
Benzo(b)fluoranthene	38	X	
Dibenz(a,h)anthracene	12.5	X	
Benzo(a)pyrene	33	X	
Dibenzo(a,i)pyrene	10	X	
Indeno(1,2,3-cd)pyrene	9	X	
Chlorinated Hydrocarbons			
1,1-Dichloroethylene	100.4		A[1]
1,1,1-Trichloroethane	99.5		A
1,1,2-Trichloroethane	99.4		A, B
1,1,2,2-Tetrachloroethane	100.7		A
Chloromethylethylether	99.7		B
1,3-Dibromo,3,chloropropane	100.5		B
Miscellaneous			
Tetraalkyllead	72.1 (as Pb)		2

[1] letters indicate compounds included in given mixture.

[2] Tetraalkyllead (TAL) was a complex gasoline sample supplied by Standard Oil Co. and consisted of 61.5% TAL, 17.9% ethylene dibromide, and 18.8% ethylene dichloride.

the beakers using a homogenization technique (Coover et al. 1987). The soils were extracted with 150 mL of solvent for 60 seconds using a Tekmar Tissumizer. A 51 percent/49 percent hexane-acetone mixture was used to extract the pesticides, while methylene chloride was used in the extractions for all other compounds. The extract was decanted from the soil (washed with water to remove acetone, when used), and was dried by passage through a column of anhydrous sodium sulfate. The extracts were concentrated, when necessary, in a Kuderna-Danish evaporator or under a gentle stream of N_2.

Abiotic controls were prepared by spiking the soil microcosms with a $HgCl_2$ solution as described by Fowlie and Bulman (1986). This method renders the soil microbially inactive while producing minimal changes in the physical and chemical properties of the soils. Abiotic control microcosms were spiked with the test substances, incubated, and extracted following the same procedures as the nonsterilized microcosms.

In addition to the individual chemicals that were tested, one complex waste sample containing toxaphene was evaluated. The toxaphene waste was added to 5 kg of Kidman sandy loam at a 0.1 percent by weight application rate. The soil/waste mixture was tumbled overnight to ensure uniform distribution of the toxaphene in the test soil. The mixture was divided into 100 g aliquots which were placed in 700 mL glass beakers for incubation. Deionized water was added to the samples to reach a water content of -0.3 bar matric potential, mixed thoroughly, incubated, and sampled as described above.

Determination of Volatilization Corrected Degradation Rates

The procedure for measuring short term (48-100 hours) volatile losses of a compound from soil was taken from the Permit Guidance Manual on

Hazardous Waste Land Treatment Demonstrations (USEPA, 1986b). The chemicals included in this phase of the study are listed in Table 8. The experimental apparatus used for volatilization measurements consisted of 500 mL Erlenmeyer flask soil reactors (Figure 1) that were used to simulate the air/soil surface environment.

A representative sample of Kidman or McLaurin soil (250 g air dried) was placed in the test reactors. The soil was initially wetted to a soil water content corresponding to a matric potential of approximately -0.33 bar. The reactors were placed in the dark and incubated at room temperature for approximately one week. Following this initial incubation period, test compounds were added individually or in a mixture in 30 mL methanol to the soil in the reactor to achieve the desired initial soil concentration. The soil was then mixed thoroughly to achieve a uniform distribution of the chemical in the soil and the flask units were immediately capped. Loading rates are listed in Table 8. All experiments included soil blank controls (without waste addition), abiotic soil controls, and duplicate soil-chemical reactors under a given set of loading and soil environmental conditions.

Once capped, the flask unit was purged with air at a controlled rate of 250 to 300 mL/min. High quality breathing air was used as the purge gas to eliminate the possibility of oxygen limitation and subsequent impact to microbial processes occurring during the experiment. Emission measurements were made by drawing a constant volume split stream sample of flask effluent gas through the sampling/collection system via a constant volume sample pump and a balanced, capillary flow controlled, four-place sampling manifold (three samples plus a blank). Use of this procedure allowed the concurrent sampling of all flask units for the same length of

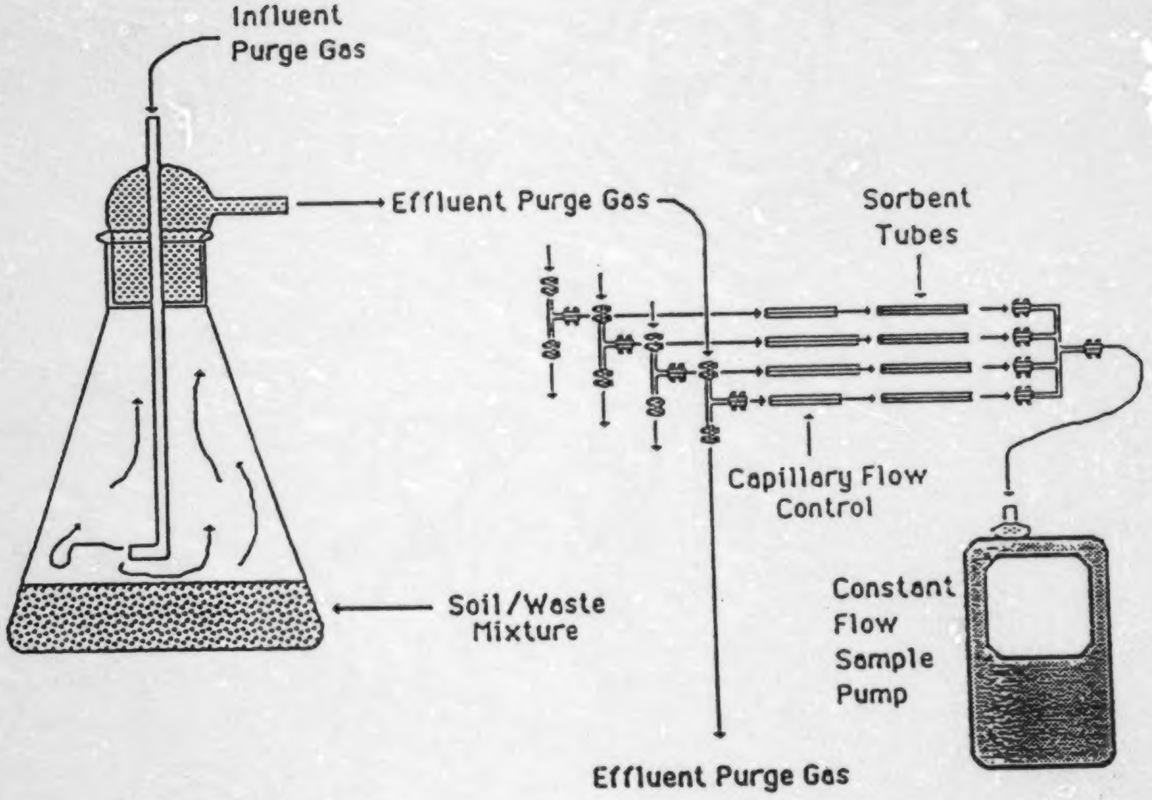

Influent Purge Gas
Effluent Purge Gas
Sorbent Tubes
Capillary Flow Control
Soil/Waste Mixture
Constant Flow Sample Pump
Effluent Purge Gas

Figure 1. Laboratory flask apparatus used for mass balance measurements.

time and during the same time period during a given volatilization experiment. The sample pump rate and purge gas flow rate were measured before each sampling event via a bubble tube flow meter. The duration of sorbent tube sampling was recorded to allow accurate soil loss rate calculations.

Sorbent tubes were sampled at a rate of 20 to 30 mL/min/trap for a period of time ranging from 0.5 minutes just after waste application to 5 minutes at the end of the volatilization experiments. Breakthrough traps were used in all sampling events to allow quantification of breakthrough which occurred during the experiments. Observed breakthrough values were reported, and all mass flux values were calculated with the inclusion of this observed breakthrough mass. Upon completion of the sampling event, the Tenax sorbent tubes were removed from the sampling system and were placed in muffled culture tubes with Teflon lined caps and stored at or below 4°C prior to thermal desorption and GC-FID analysis.

A modification of Method 5030 "Purge-and-Trap Method" (U.S. EPA 1982) was used for the extraction of soils used in the volatilization study. The method involves the extraction of 2 to 5 g of soil with approximately 35 mL of distilled-in-glass methanol. The soil/methanol mixture is placed in screw-top centrifuge tubes without a headspace and is vortexed for two minutes. The mixture is then centrifuged at 2000 rpm for 20 minutes, and the centrate is stored in Teflon^{TM} screw-top vials at or below 4°C prior to analysis by GC-FID.

The sampling and analysis procedure for both gas and soil samples was repeated at selected time intervals following compound addition corresponding to the anticipated log decay in compound emission rates.

The general sampling schedule used for emission measurements and soil flask sacrifice and extraction was as follows:

0, 15 min, 1 hr, 2.5 hrs, 10 hrs, 25 hrs, 50 hrs, 100 hrs.

Sorbent tube and soil extraction blanks and spikes were used throughout the study to provide adequate method QA/QC. Soil drying was minimized by bubbling the purge gas through distilled deionized water before entering the microcosm units.

Analytical Methods for Determination of Substance Concentration in Soil Systems

Analytical methods used for the identification and determination of the concentration of substances in the test systems, including soil and air phases, are given in Table 9. Instrumentation and analytical conditions are presented. All analytical methods were based on EPA procedures given in Test Method for Evaluating Solid Wastes, Physical/Chemical Methods (U.S. EPA 1982).

Soil Sterilization - Enumeration of Soil Microbes

Beakers of soil were prepared as described above, with and without the addition of $HgCl_2$. Plate counts of soil microorganisms including bacteria, actinomyces and fungi were performed following the procedure of Wollum (1983). Microorganism counts were performed over a period of 30 days to determine effectiveness of $HgCl_2$ for sterilizing soil.

Data Calculations

Degradation kinetic parameters and half-life ($t_{1/2}$ in days) values were calculated from specific constituent soil concentration and vapor flux data. Mean concentrations for replicate soil flask units were used in all calculations.

TABLE 9. CHEMICAL IDENTIFICATION AND QUANITIFICATION METHODS AND CONDITIONS

Compound	Method of Analysis	Detector	Column	GC/HPLC column conditions
4,4'-DDT	GC	ECD	1	1
Aniline	GC	NPD	2	3
Pentachloronitrobenzene	GC	ECD	1	1
Trichlorobenzene	GC	ECD	1	2
3-methylcholanthrene	HPLC	UV	3	6
Acenaphthylene	HPLC	UV	3	6
Aldicarb	HPLC	UV	3	5
Dinoseb	HPLC	UV	3	6
Famphur	HPLC	UV	3	5
Pronamide	HPLC	UV	3	6
Warfarin	HPLC	UV	3	5
Benz[a]anthracene	HPLC	UV	4	7
Benz[a]pyrene	HPLC	UV	4	7
Chrysene	HPLC	UV	4	7
Dibenzo[a,h]anthracene	HPLC	UV	4	7
Indeno(1,2,3-cd)pyrene	HPLC	UV	4	7
Flouranthene	HPLC	UV	4	7
Naphthalene	GC	FID	2	2
1-Methylnaphthalene	GC	FID	2	2
Phenanthrene	HPLC	UV	4	7
Pyrene	HPLC	UV	4	7
Benzo[b]fluoranthene	HPLC	UV	4	7
Dibenzo[b]pyrene	HPLC	UV	4	7
7,12-Dimethylbenzanthracene	HPLC	UV	4	7
1,1-Dichloroethylene	GC	FID	5	4
1,1,1-Trichloroethane	GC	FID	5	4
1,1,2,2-Tetrachloroethane	GC	FID	5	4
1,1,2-Trichloroethane	GC	FID	5	4
1,2,4-Trichlorobenzene	GC	ECD	1	2

Column legend
1= DB-5 15 m x 0.53 mm I.D. capillary column (J&W Scientific), flow rate: 5mL/min Nitrogen
2= 3% 2250 1.5 m x 2mm I.D. packed glass column (Supelco), flow rate: 30 mL/min Helium
3= C-18 (5µm packing), 250 x 4mm (SGE)
4=ODS (5µm packing), 150 x 4 mm (Supelco, LC-PAH)
5=1% SP 1000 3m x 2 mm I.D. packed glass column (Supelco), flow rate: 30 mL/min Helium

GC column temperature condition legend
1=190°C for 1min, 12°C/min to 220°C, hold for 5 min
2=120°C isothermal
3= 90°C isothermal
4=100°C for 5 min, 8°C/min to 225°C, hold for 20 min

HPLC column conditions
5= Mobile phase: water:acetonitrile, 49% ACN to 90% ACN, hold 2 min., flow rate: 2ml/min,
6= Mobile phase: water:acetonitrile, 50%ACN to 100%ACN, hold 3 min, flow rate: 2mL/min,
7= Mobile phase: water:acetonitrile, 40% ACN to 100% ACN, hold 2 min., flow rate: 2ml/min.

Detector operating conditions
ECD = electron capture detector, Temperature 300 °C, total flow (makeup + column)= 35 mL/min
FID = flame ionization detector, Temperature = 300 °C, Hydrogen flow = 40 mL/min, air flow = 400 mL/min
NPD = nitrogen-phosphorous detector, temperature = 300 °C, hydrogen flow = 3 mL/min, air flow = 120 ml/min
UV = ultraviolet detector, wavelength = 254 nm

Degradation Kinetics--

For each constituent investigated, rate constants and t1/2 values were calculated assuming first order kinetics. For those compounds for which degradation rates were not corrected for volatilization, no modifications to the measured constituent soil mass values were required. The integrated form of the first order rate expressions was used to determine the first order rate constant, k_1, and t1/2 values. For first order kinetics, the rate coefficient was determined from a least squares regression of the natural log transformation of constituent soil concentration at time t divided by the initial constituent soil concentration, ln(Ct/Co), versus time. Half-life ($t_{1/2}$) values are calculated based on the time to reach a constituent soil concentration equal to 1/2 the initial concentration, $(\ln(0.5)/-k_1 = -0.693/-k_1 = t_{1/2})$. For those compounds for which volatilization losses were monitored, constituent soil loss data were modified as described below to provide volatile loss corrected k_1 and $t_{1/2}$ values.

Volatilization Corrected Degradation Rates--

For those constituents for which volatilization rates were measured, the calculation of a degradation rate corrected for this volatile loss was carried out using the difference form of the first order degradation rate equation:

$$dM/dt = -kM \qquad (1)$$

Use of this equation requires the calculation of the change in degraded mass over time, along with the mean mass of constituent over a specific time interval, dt. This procedure is summarized below:

1) An emission rate was determined for each constituent at each sampling interval taking into account the duration of each sampling event,

the fraction of purge flow actually sampled, and the mass collected during sampling, corrected for breakthrough and method recovery efficiency:

$$\text{Emission Rate}_t = \frac{\text{Mass collected in vapor}}{\text{Duration of sample}} * \frac{\text{Purge air flowrate}}{\text{Sample air flowrate}} \qquad (2)$$

2) The total emitted mass collected over consecutive sampling times was calculated from the product of the mean of the emission rates at each sampling time and the length of time between consecutive sampling events:

$$\begin{array}{l}\text{Cumulative} \\ \text{Emitted} \\ \text{Mass } t_{i+1}-t_i\end{array} = (\text{Emission Rate}_{i+1} + \text{Emission Rate}_t)/2*(t_{i+1}-t_i) \qquad (3)$$

3) The soil constituent mass if no degradation had occurred was calculated as the difference between the constituent mass added to the soil at time t=0 and the measured cumulative volatilized mass at each sampling time corrected for method recovery:

$$\begin{array}{c}\text{Soil Constituent} \\ \text{Mass if Not} \\ \text{Degraded}_t\end{array} = \text{Constituent Mass}_{t=0} - \text{Cumulative Emitted Mass}_t \qquad (4)$$

4) The mass degraded was calculated as the difference between the soil mass calculated from Equation 4 and the actual constituent soil concentration at each sampling time corrected for method recovery:

$$\begin{array}{c}\text{Soil Constituent} \\ \text{Mass Degraded}_t\end{array} = \begin{array}{c}\text{Soil Constituent} \\ \text{Mass If Not Degraded}_t\end{array} - \begin{array}{c}\text{Actual Constituent} \\ \text{Soil Mass}_t\end{array} \qquad (5)$$

5) The mean constituent soil mass over each sampling increment was calculated as the arithmetic mean of constituent soil mass values measured at each sampling time.

6) The change in degraded mass between consecutive sampling times was divided by the length of time of each increment to provide calculated

values for dM/dt:

$$dM/dt = \frac{\begin{matrix}\text{Soil Constituent} \\ \text{Mass Degraded}\end{matrix}_{t+1} - \begin{matrix}\text{Soil Constituent} \\ \text{Mass Degraded}\end{matrix}_{t}}{(t+1-t)} \qquad (6)$$

7) Volatilization corrected degradation rate values, k, were then calculated from a linear regression of dM/dt versus mean constituent mass M, over each time interval, as given from Equation 1.

PARTITION COEFFICIENT DETERMINATIONS

Calculational Approach for Partition Coefficients Based on Structure-Activity Relationships

Partition coefficients between aqueous and soil (K_d), oil (K_o), and air (K_h) phases were estimated for the chemicals listed in Tables 1 through 3. The following methods were used:

Estimation of K_d—

The partition coefficient of a chemical between soil and water is given by:

$$K_d = C_s/C_w \qquad (7)$$

where K_d is the soil/water partition coefficient (unitless if C_s and C_w are in the same units), C_s is the concentration of chemical in the soil phase, and C_w is the concentration of chemical in the aqueous phase.

K_d values for a soil can be estimated from K_{oc} values if the organic fraction of the soil, f_{oc}, is known and if it is assumed that hydrophobic interactions dominate the partitioning process:

$$K_d = K_{oc}f_{oc} \qquad (8)$$

where K_{oc} is the organic carbon normalized soil/water partition coefficient.

By assuming that partitioning between water and the organic fraction of soil is similar to partitioning between octanol and water, several correlation equations have been developed which relate K_{OC} to octanol/water partition coefficients (K_{OW}). The correlation equation used to calculate K_{OC} for this project was that of Karickhoff et al. (1979):

$$\log K_{OC} = 1.0 \log K_{OW} - 0.21 \qquad (9)$$

Experimental values of log K_{OW} obtained from the literature were used when available. Log K_{OW} values, estimated using the fragment approach of Hansch and Leo (1979), were used when experimental values were not available.

The second approach employed for the estimation of log K_{OC} was based on molecular connectivity indexes (MCIs). MCIs are topological parameters which describe the degree of bonding or connectedness of the nonhydrogen atoms in a molecule. First order MCIs (${}^{1}x$), calculated from the molecular structure of a compound, have been shown to be highly correlated with soil/water partition coefficients (Sabljic, 1984; Sabljic, 1987).

First order MCIs were calculated using a computer program written in Fortran for an Apple Macintosh computer. The K_{OC} values were calculated from the first order MCI using the regression equation developed by Sabljic (1987):

$$\log K_{OC} = (0.53)\ {}^{1}x + 0.54 \qquad (10)$$

The resultant K_{OC} values were used along with percent organic carbon values to calculate K_d values of the Kidman and McLaurin soils using equation 8.

Estimation of K_o—

The partition coefficient of a chemical between water and oil is given by:

$$K_o = C_o/C_w \qquad (11)$$

where K_o is the oil/water partition coefficient (unitless if C_o and C_w are in the same units), C_o is the concentration of chemical in the oil phase, and C_w is the concentration of chemical in the water phase.

K_o values were estimated using a correlation expression between K_o and K_{ow} given by Leo and Hansch (Leo et al. 1971). This equation, developed using olive, cottonseed, and peanut oils, is presented below after solving for log K_o:

$$\log K_o = 1.12 \log K_{ow} - 0.324 \qquad (12)$$

Estimation of K_h—

The partition coefficient of a chemical between air and water can be written as:

$$K_h = C_a/C_w \qquad (13)$$

where K_h is the air/water partition coefficient, C_a is the concentration of chemical in the air phase, and C_w is the concentration of chemical in the aqueous phase.

K_h can also be expressed as a dimensionless Henry's Law constant H/RT. Values of H can be calculated from the ratio of a chemical's vapor pressure to its aqueous solubility if it is assumed that the liquid phase activity coefficients are constant up to the solubility limit. Using experimental values for vapor pressure (P_v) and aqueous solubility (S) obtained from the literature, K_h was calculated using the following expressions:

$$K_h = H/RT = (P_v/S)/RT \qquad (14)$$

where P_v is the vapor pressure (torr), S is aqueous solubility (moles/liter), R is the gas constant (62.3 liter torr/atm K) and T is temperature (298°K).

If literature values of P_v or S were unavailable for a particular compound but boiling point and melting point values were available, Pv values were estimated using the following expression developed by MacKay et al. (1982).

$$\ln P_V = -(4.4 + \ln T_B)\ [1.803(\frac{T_B}{T} - 1)] - 0.803 \ln \frac{T_B}{T} - 6.8(\frac{T_M}{T} - 1) \qquad (15)$$

where P_V is in torr and T_B, TM and T are the boiling point, melting point and an environmental temperature (°K), respectively.

QA/QC PROCEDURES FOR DEGRADATION AND PARTITION EXPERIMENTS

Soil spiking and recovery studies were conducted to determine the effects of soil, test substance, and soil/test substance matrix on constituent extraction and recovery efficiency. Extracts of the soil and complex wastes were spiked with test substance(s) of interest to evaluate the effect of these matrices on constituent identification and quantification. Interferences due to the extract matrix were identified.

Standard solutions were prepared using primary standards of the test substance dissolved in a suitable solvent that did not interfere with constituent identification and quantification. Standard curves were generated using at least six points ranging from the highest concentration anticipated to the detection limit for the constituent.

MATHEMATICAL MODEL FOR SOIL-WASTE PROCESSES

A mathematical description of a land treatment system, based upon a conceptual model of the land treatment process, that incorporates specific requirements for the land treatment demonstrations specified by the U.S. Environmental Protection Agency (EPA) in 40 CFR Part 264.272 provides a framework for integrating and evaluating the relevant information. Specifically this includes: (1) evaluation of literature and/or experimental data for the selection of constituents most difficult to treat, considering the combined effects of degradation and immobilization (principal hazardous constituents, PHCs), (2) evaluation of the effects of site characteristics on treatment performance (soil type, soil horizonation, soil permeability), (3) determination of the effects of design and operating parameters (loading rate, etc.) on treatment performance, (4) evaluation of the effects of environmental parameters (season, precipitation), and (5) comparison of the effectiveness of treatment using different design and management practices in order to maximize treatment.

The values developed for degradation (or apparent loss) and immobilization for pesticides in the treatability studies were used as input for the mathematical models VIP and RITZ. The VIP model (Vadose Zone Interactive Processes) is an enhanced version of the mathematical model RITZ (Regulatory and Investigative Treatment Zone Model), developed by the U.S. EPA, Robert S. Kerr Environmental Research Laboratory (Short 1986), for quantitatively integrating the processes of degradation and immobilization in the unsaturated zone of a soil system. The VIP model was developed at Utah State University for use in evaluation of site-specific treatment potential for specific waste-soil mixtures, and for determination of the potential for migration of hazardous constituents from a site to groundwater and to the atmosphere and is described by Grenney et al. (1987). The VIP model has been used to rank organic hazardous constituents with respect to tendencies to leach and to volatilize, and, therefore, to indicate the relative soil assimilative capacities (SAC) for a group of hazardous organic constituents (Grenney et al. 1987, McLean et al. 1987).

VIP incorporates the assumptions described by Short (1986). The major differences between RITZ and VIP are the numerical solution algorithms used in VIP and the option to use nonequilibrium kinetics in

VIP. Use of the numeric solution algorithm is an enhancement allowing the input of pollutant concentration profiles in any phase as the initial conditions, monthly variations or recharge, temperature, and pollutant application at user defined intervals.

The same input parameters and initial conditions were used in both model simulations, and results of the outputs of the models were evaluated and compared. Therefore, for the VIP model the following input parameters were used: (1) initial conditions were set to zero (no initial chemical concentration in soil), (2) no monthly variation of water flow (or recharge), (3) temperature in soil remains constant, and (4) chemical application occurred only once (at time = 0), (5) use of local equilibrium for partitioning of chemicals among soil, oil, air, and water phases of the soil system.

Additional information concerning the RITZ mathematical model is presented by Short (1986). A detailed description and listing of the VIP model (formerly RITZE) can be found in the Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations (U.S. EPA, 1986), Grenney et. al. (1987), and in API (1987).

TRANSFORMATION STUDIES

Soil Incubation of Dimethylbenzanthracene (DMBA)

Transformation studies were performed with the McLaurin sandy loam soil at low pH and the same soil adjusted to neutral pH for 7,12-dimethylbenzanthracene (DMBA). Soil pH was adjusted from 4.8 to 7.5 by adding 70 mg of $CaCO_3$ to the McLaurin soil. DMBA was chosen based on reported genetic toxicity (Shoza et al. 1974, Walters 1966) and the rate and extent of degradation measured in laboratory studies (Park 1987).

One hundred grams (dry weight) of soil at the water potential of -0.33 bar were placed in a 500 mL glass beaker. Following 14 days of incubation, 100 mg of DMBA was added to the soil (1000 mg/kg) in a methylene chloride solution. After the methylene solution evaporated from the soil (approximately 24 hrs), water was added to adjust the soil moisture content to -0.33 bar soil-water potential. Soil beakers were covered with polyethylene film to control soil water content. Polyethylene film is permeable to oxygen and is effective for reducing the loss of soil water while maintaining aerobic conditions (Bossert et al. 1984).

Evaporative water losses during incubation were replaced by periodic (approximately every 14 days) water addition in order to maintain soil-water potential in the range of -1 to -0.33 bar. Soil beakers were incubated at 20°C in the dark to prevent photodegradation of the PAH compound. Control experiments were performed under identical incubation conditions. Soil blanks were incubated without DMBA. Poisoned controls (2% $HgCl_2$) with and without DMBA were also prepared to monitor and account for possible abiotic transformations of soil humus and the PAH, respectively, in soil systems.

Analysis of DMBA

Soil beakers were withdrawn from the incubation units at 0, 14, and 28 days after PAH addition. The schedule of sampling times was based upon preliminary experiments and ensured that a sample would be taken beyond the chemical half-life in soil. Each beaker was extracted with 200 mL methylene chloride using a homogenization technique (Tekmar Tissue Homogenizer, Tekmar Co. Cincinnati, OH). Methylene chloride extracts were dried over anhydrous sodium sulfate and evaporated to 1 mL under an aerated hood.

An aliquot of the extract was injected into a Perkin-Elmer HPLC system fitted with a 4.6 mm I.D. x 250 mm 15-u octadecylsilane column (Supelco Inc., Bellefonte, PA) and eluted with a water/acetonitrile gradient (from 35% to 100% of acetonitrile) at a flow rate of 0.9 mL min^{-1}. The eluate was monitored using a 254 nm UV detector. Seven reference standards of hydroxylated derivatives of 7,12-dimethylbenz(a) anthracene were provided by Dr. Melvin S. Newman (Ohio State University, Columbus, OH) including; 1-hydroxy-, 2-hydroxy-, 3-hydroxy-, 4-hydroxy-, 5-hydroxy, 8-hydroxy-, and 10-hydroxy-7,12-dimethylbenz(a)anthracene. These compounds were analyzed by HPLC using the same HPLC conditions that were used for soil extracts.

Experiments with radiolabeled DMBA

Experiments with radiolabeled DMBA were conducted as described above except 2 uCi (12-^{14}C)DMBA was added to 10 g (dry weight) of the McLaurin sandy loam soil (0.2 uCi g^{-1}). (12-^{14}C)DMBA was purchased from Amersham Corp. (Arlington Heights, IL) with a specific radioactivity of 8.3 mCi/mmol, and radiochemical purity of 97%.

The distribution of $^{14}CO_2$ between evolved CO_2, soil extracts, and soil residue components was measured to construct a mass balance for DMBA. Soil samples were extracted at 0, 14, and 28 days after application of DMBA. The extracted soil was air dried and stored in a refrigerator prior to analysis for soil residue ^{14}C. The extract was dried over anhydrous sodium sulfate and concentrated to 1 mL under an aerated hood.

The sample extracts (100 uL) were chromatographed on an HPLC system using the same conditions and methods as described in the analysis of

DMBA. Fractions of the HPLC eluate (0.25 mL) were collected at 1 min intervals and added to tubes containing 3.5 mL of scintillation liquid. The radioactivity present in each fraction was determined in a Beckman LS 5801 liquid scintillation counter (Beckman Instruments Inc., Carlsbad, CA). Corrections were made for machine efficiency and quenching.

A sample of the extracted soil (0.1 g) was combusted at 700 C in a stream of O_2 in a Biological Material Oxidizer (BMO/R.J. Harvey Instrument Corp.). After catalytic oxidation of combustion gases, the CO_2 produced was trapped in a solution of a 2:1 mixture of Carbasorb (Packard Instrument) and Scintiverse II (Fisher Scientific). The trapping solution was then counted for ^{14}C.

The mineralization of ^{14}C DMBA in the soil was determined using a flask which has CO_2 trapping liquid. Solutions of KOH (0.1 N) were used for trapping the evolved CO_2. Trapped $^{14}CO_2$ was quantified by liquid scintillation counting. KOH solutions in the CO_2 traps were changed once a week during the 28-day incubation period.

Mutagenicity Evaluation

Soil samples were incubated and extracted as described previously except 1000 g (dry weight) of DMBA treated soils (1000 mg/kg) were placed in a 3 L glass beaker. A large amount of soil (1000 g) was used in order to obtain sufficient amounts of DMBA metabolites (weight of metabolites) for the Ames mutagenicity assay. Soil extracts were separated into three metabolite fractions based on HPLC retention time (polarity) (0-15 min, 15-33 min, and 35-45 min) and isolated by preparative scale HPLC on a 21.2 mm I.D. x 250 mm 15-u octadecylsilane column (Supelco Inc., Bellefonte,PA) using a water/acetonitrile gradient (35%-100%) at a flow rate of 8 mL/min. The HPLC fractions were evaporated to dryness under an aerated hood and reconstituted with dimethylsulfoxide (DMSO).

Mutagenicity of DMBA and metabolite fractions were measured with the Ames assay (Ames et al. 1975; Maron and Ames, 1983; and U.S. EPA, 1983b) using the Salmonella typhimurium strain TA-100. Salmonella strain TA-100, which detects mutagens causing base-pair substitutions, was supplied by Dr. Bruce N. Ames (University of California, Berkeley, CA). Samples were tested on triplicate plates in the standard plate incorporation assay at four dose levels with enzyme activation (S9), and 2-Aminofluorene (10 ug/plate) was used as a positive control. Mutagenic potential of each test sample was expressed as the mutagenic ratio (MR), i.e., ratio of number of colonies in the presence of a test sample to the number of colonies on a control growth plate in the absence of the test sample.

SECTION 5

RESULTS AND DISCUSSION

QUALITY CONTROL/QUALITY ASSURANCE

Soil Sterility Controls

Figures 2 and 3 show microbial counts, including bacteria, actinomycetes, and fungi, for the Kidman and McLaurin soils with and without $HgCl_2$ treatment. $HgCl_2$ treatment was effective in reducing the microbial population in both soils to less than ten organisms per gram of soil. Generally a five log reduction in the number of bacteria and a two to four log reduction in the number of soil fungi was achieved using $HgCl_2$.

Extraction Efficiencies

Initial recovery efficiency data are shown in Tables 10-12. Extraction efficiencies were in general greater than 80 percent. Exceptions include volatile constituents and aniline, hexachlorocyclopentadiene and 1,2,4-trichlorobenzene (McLaurin soil only). The later three compounds are volatile, making solvent extraction difficult.

The addition of $HgCl_2$ did not effect extraction recoveries for most compounds evaluated (Tables 10-12). The recoveries of phorate, parathion, methyl-parathion, disulfoton, famphur, and pronamide in the presence of $HgCl_2$ were, however, less than 10 percent. Recovery studies were repeated with these compounds to determine whether the mercury reacted directly with the chemical. When the chemicals were added to distilled water samples with and

Figure 2. Microbial plate counts for untreated and $HgCl_2$ treated Kidman soil.

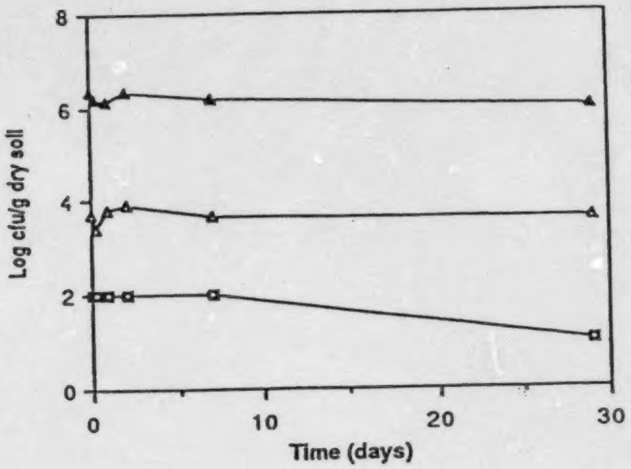
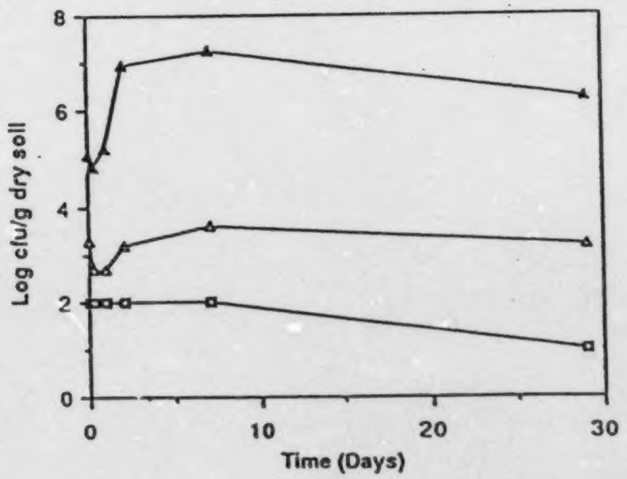


Figure 3. Microbial plate counts for untreated and $HgCl_2$ treated McLaurin soil.



-▲- = bacterial and actinomycetes colony forming units (cfu) in non-treated soil.

-△- = fungal cfu in non-treated soil.

-□- = highest possible number of fungal, bacterial and actinomycetes cfu in soil treated with a 2% $HgCl_2$ solution.

TABLE 10. EXTRACTION EFFICIENCIES FOR PAHs FROM MCLAURIN AND KIDMAN SOILS

Chemical	Soils							
	McLaurin				Kidman			
	% Recovery							
	Without $HgCl_2$		With $HgCl_2$		Without $HgCl_2$		With $HgCl_2$	
	Average*	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
Acenaphthylene	77.1	4.6	74.7		58.6	4.9	56.1	
3-methylcholanthrene	84.8	2.7	86.1		98.4	7.8	92.5	
Naphthalene	37.9	9.4	80.8	3.8	85.5	3.2	79.6	3.9
1-methylnaphthalene	91.2	12.9	82.1	3.7	85.1	4.5	83.5	2.9
Anthracene	95.8	2.0	91.7	5.0	85.7	2.6	90.9	5.0
Phenantherene	97.1	6.7	95.3	4.4	90.7	4.7	93.6	3.2
Fluoranthene	89.0	3.5	88.8	5.5	88.8	0.90	88.9	1.4
Pyrene	91.4	5.0	91.3	2.9	83.2	4.5	87.7	3.0
Chrysene	94.1	4.4	91.2	2.6	90.0	3.8	92.3	2.9
Benz(a)anthracene	91.2	3.3	88.6	3.8	82.1	3.4	84.2	4.0
7,12-dimethylbenz (a)anthracene	81.7	3.3	87.2	2.1	77.3	2.1	79.1	3.9
Benzo(b) fluoranthene	89.4	3.9	88.3	2.3	79.0	2.0	80.7	3.8
Dibenz(a,h) anthracene	90.9	3.7	89.6	1.4	79.6	2.6	83.2	1.9
Benzo(a)pyrene	90.1	2.0	91.2	2.7	81.2	2.3	81.7	3.8
Dibenzo(a,i) pyrene	92.2	1.9	90.3	3.0	80.2	2.1	79.1	3.0
Indeno(a,2,3-cd) pyrene	91.2	4.0	90.8	3.7	90.9	1.8	91.9	2.4

* n = 3

TABLE 11. EXTRACTION EFFICIENCIES FOR PESTICIDES FROM MCLAUREN AND KIDMAN SOILS

Chemical	Soils						
	McLaurin			Kidman			
	% Recovery						
	Without $HgCl_2$		With $HgCl_2$	Without $HgCl_2$		With $HgCl_2$	
	Average*	Std. Dev.	Average	Average	Std. Dev.	Average	Std. Dev.
Aldrin				96.0	1.8	89.4^{+}	
Heptachlor	94.2	3.7	71.4^{+}	88.2	2.6	95.7^{+}	
Endosulfan				84.5	1.9	61.3^{+}	
Toxaphene				81.5+			
Parathion				79.2	2.5	0^{+}	
Methyl-parathion				65.1	4.1	0^{+}	
Phorate	88.9	10.3	0^{+}	87.1	1.8	0^{+}	
Disulfoton				98.4	2.0	0^{+}	
Dinoseb	89.1	3.8	87.1	100.3	7.8	90.8	
Pronamide	84.3	4.0	0^{+}	86.0	6.6	0^{+}	
Aldicarb	100.2	1.5	93.4	100.2	1.0	104.3	
Famphur	99.9	3.0	8.5	83.6	4.0	7.5	
Warfarin	124.7	4.4	88.8	120.3	4.5	93.5	
DDT	90.1	5.3	131.0^{+}	114.0	20.1	162.0^{+}	
Lindane	69.1	1.8	78.0^{+}	79.9	2.1	89.4^{+}	
Pentachloronitro-benzene	81.0	3.8	247^{+}	88.8	25.7	273^{+}	

* n = 3

+ n = 2

TABLE 12. EXTRACTION EFFICIENCIES FOR THE CHLORINATED HYDROCARBONS AND MISCELLANEOUS COMPOUNDS FROM MCLAURIN AND KIDMAN SOILS

Chemical	Soils					
	McLaurin			Kidman		
	% Recovery					
	Without $HgCl_2$		With $HgCl_2$	Without $HgCl_2$		With $HgCl_2$
	Average*	Std. Dev.	Average	Average	Std. Dev.	Average
1,2,4-trichloro-benzene	40.0	8.1	33.1+	123.0	23.8	123.0+
Aniline	30.3	6.5	50.8	20.7	2.2	40.6
Hexachlorocyclo-pentadiene	11.5	2.78	23.4+	15.0	1.80	41.3+
1,1-cichloroethylene	19.7#	6.4				
1,1,1-trichloroethane	32.4#	3.9				
1,1,2-trichloroethane	58.2#	10.4				
1,1,2,2-tetrachloro-ethane	53.4#	24.0				

* n = 3
+ n = 2
# n = 6

without $HgCl_2$ (no soil was used), and the samples were immediately extracted and analyzed, recoveries for samples without $HgCl_2$ were 80-90 percent, while recoveries for samples with $HgCl_2$ were again less than 10 percent. Intermediate breakdown products, determined by GC/MS, for pronamide and famphur in the presence of $HgCl_2$ are shown in Figure 4. As indicated in Figure 4, for the compound famphur, organophosphates may undergo oxidation in the presence of mercury to form the oxygen analog of those compounds. It is speculated that mercury directly catalyzed the breakdown of the reactive side chains of these pesticides. Mercuric chloride, while providing excellent and continuous sterilization of soils used in this investigation, is not recommended for use with compounds that are chemically reactive based on results obtained for pronamide and famphur.

Extraction recoveries for DDT, and pentachloronitrobenzene (PCNB) in the presence of $HgCl_2$ were greatly enhanced, with recoveries in excess of 150 percent. Soil blanks, with and without $HgCl_2$, were analyzed. There was no significant difference between the soil blanks. The presence of DDD and DDE in the Kidman soil blank indicated previous agricultural use of the soil, even though the soil had been left fallow for the last 10 years. The actual concentrations of DDD and DDE were, however, insignificant compared with the DDT added and would not account for enhanced recovery efficiencies. The high extraction recoveries of DDT and PCNB in the presence of $HgCl_2$ may be due to analytical error.

Degradation of PAH Constituents

Cumulative volatilized mass for PAH compounds was calculated after 48 hours of incubation. Data are presented in Table 13 for Kidman fine sandy loam and McLaurin sandy loam soils. Volatilization loss of naphthalene and 1-methylnaphthalene was substantial for both soils. No significant volatilization was observed for the other PAH compounds investigated.

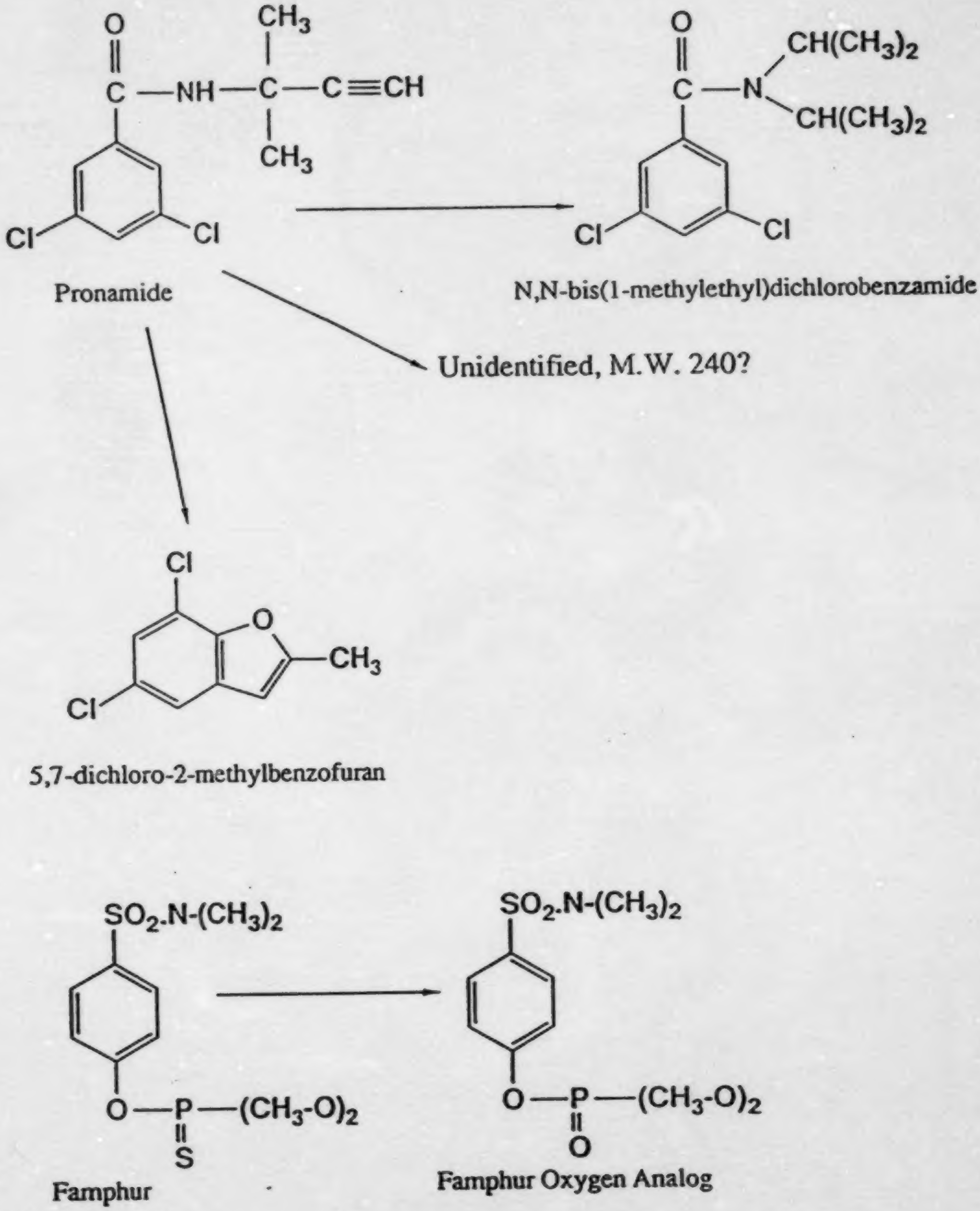

Pronamide
N,N-bis(1-methylethyl)dichlorobenzamide
Unidentified, M.W. 240?
5,7-dichloro-2-methylbenzofuran
Famphur
Famphur Oxygen Analog

Figure 4. Intermediate breakdown products for pronamide and famphur identified from GC/MS results.

TABLE 13. VOLATILIZATION OF PAH COMPOUNDS FROM KIDMAN AND MCLAURIN SOILS

Compound	Percent Volatilized Kidman	 McLaurin
Naphthalene	32.3	29.2
1-Methylnaphthalene	14.7	26.9
Anthracene	<0.1	<0.1
Phenanthrene	<0.1	<0.1
Fluoranthene	b.d.[a]	b.d.
Pyrene	b.d.	b.d.
Chrysene	b.d.	b.d.
Benz(a)anthracene	b.d.	b.d.
7,12-Dimethylbenz(a)anthracene	b.d.	b.d.
Benzo(b)fluoranthene	b.d.	b.d.
Dibenz(a,h)anthracene	b.d.	b.d.
Benzo(a)pyrene	b.d.	b.d.
Dibenzo(a,i)pyrene	b.d.	b.d.
Indeno(1,2,3-cd)pyrene	b.d.	b.d.

[a] Collected mass below detection.

Volatilization corrected PAH degradation information was obtained by subtracting the total of cumulative volatilized mass and mass of PAH compounds remaining in the soil from the mass of compounded added. Volatilization corrected degradation kinetic results for the PAH compounds in Kidman and McLaurin soils are summarized in Tables 14 and 15, respectively. Degradation kinetics are expressed as first-order reaction rates (k_1) and as half-lives ($t_{1/2}$) for each soil.

The degradation of two-ring PAH compounds, naphthalene and 1 methyl-naphthalene, was extensive. Half lives for these PAH compounds were approximately two days. The degradation of three-ring PAHs, anthracene and phenanthrene, was also extensive. Anthracene, however, was degraded more slowly than phenanthrene. The extensive degradation of these two- and three-ring PAH compounds is not unexpected because these compounds can be utilized as a sole source of carbon and energy for soil microorganisms (Davies and Evans 1964, Dean-Raymond and Bartha 1975, Evans et al. 1965). The four-, five-, and six-ring PAH compounds were somewhat recalcitrant. It has been demonstrated that natural soil microorganisms can degrade these PAHs by co-metabolic processes (Sims and Overcash 1983). The relative stability of these PAH compounds in this study suggests that the resident microbial distribution in the soils used may not have included organisms capable of degrading these compounds or a suitable substrate was not present to stimulate co-metabolic decomposition. 7,12-dimethylbenz(a)anthracene was extensively degraded with average half-lives of 20 days and 28 days for Kidman and McLaurin soils respectively.

The results (Tables 14 and 15) generally indicated that PAH persistence increased with increasing molecular weight or compound ring number. These results are consistent with the results of other studies using complex wastes (Sims et al. 1986). However, higher molecular weight PAH compounds were observed to be more resistant to degradation when present as pure compounds in soil in this study than when present at the same concentrations in the same soil in complex waste mixtures (Sims et al. 1986).

The behavior of PAH compounds in Kidman and McLaurin soil samples poisoned by 2 percent $HgCl_2$ are presented in Table 16. Statistical analysis of the data indicated that the extent of degradation of two-ring and three-ring compounds was small but significant at a significance level of 95 percent ($p < 0.05$). Since 2 percent $HgCl_2$ effectively suppressed

TABLE 14. VOLATILIZATION CORRECTED DEGRADATION KINETIC INFORMATION FOR PAH COMPOUNDS APPLIED TO KIDMAN SANDY LOAM AT -0.33 BAR SOIL MOISTURE

Compound	n	C_o (mg/kg)	k (day^{-1})	$t_{1/2}$ (days)	r^2	95% Confidence Interval			
						Lower Limit		Upper Limit	
						k (day^{-1})	$t_{1/2}$ (days)	k (day^{-1})	$t_{1/2}$ (days)
Naphthalene	12	101	-0.3370	2.1	0.883	-0.4190	1.7	-0.2550	2.7
1-Methylnaphthalene	12	102	-0.4150	1.7	0.922	-0.4960	1.4	-0.3350	2.1
Anthracene	15	210	-0.0052	134	0.829	-0.0065	106	-0.0038	182
Phenanthrene	12	902	-0.0447	16	0.952	-0.0514	13	-0.0380	18
Fluoranthene	15	883	-0.0018	377	0.724	-0.0025	277	-0.0012	578
Pyrene	15	686	-0.0027	260	0.708	-0.0036	193	-0.0017	408
Chrysene	15	100	-0.0019	371	0.804	-0.0024	289	-0.0013	533
Benz(a)anthracene	15	107	-0.0026	261	0.855	-0.0033	210	-0.0020	347
7,12-Dimethylbenz(a) anthracene	12	18	-0.0339	20	0.944	-0.0394	18	-0.0284	24
Benzo(b)fluoranthene	15	39	-0.0024	294	0.830	-0.0030	231	-0.0018	385
Benzo(a)pyrene	15	33	-0.0022	309	0.769	-0.0029	239	-0.0015	462
Dibenz(a,h)anthracene	15	12	-0.0019	361	0.726	-0.0026	267	-0.0013	533
Dibenzo(a,i)pyrene	15	11	-0.0019	371	0.746	-0.0025	277	-0.0013	533
Indeno(1,2,3-cd)pyrene	15	8	-0.0024	288	0.793	-0.0031	224	-0.0017	408

TABLE 15. VOLATILIZATION CORRECTED DEGRADATION KINETIC INFORMATION FOR PAH

COMPOUNDS APPLIED TO MCLAURIN SANDY LOAM AT -0.33 BAR SOIL MOISTURE

Compound	n	C_o (mg/kg)	k (day^{-1})	$t_{1/2}$ (days)	r^2	95% Confidence Interval			
						Lower Limit		Upper Limit	
						k (day^{-1})	$t_{1/2}$ (days)	k (day^{-1})	$t_{1/2}$ (days)
Naphthalene	12	101	-0.3080	2.2	0.786	-0.4150	1.7	-0.2020	3.4
1-Methylnaphthalene	12	106	-0.3210	2.2	0.809	-0.4240	1.6	-0.2170	3.2
Anthracene	15	199	-0.0138	50	0.932	-0.0164	42	-0.0113	61
Phenanthrene	12	893	-0.0196	35	0.808	-0.0259	27	-0.0132	53
Fluoranthene	15	913	-0.0026	268	0.575	-0.0040	173	-0.0011	630
Pyrene	15	697	-0.0035	199	0.609	-0.0053	131	-0.0017	408
Chrysene	15	105	-0.0018	387	0.610	-0.0027	257	-0.0008	866
Benz(a)anthracene	15	99	-0.0043	162	0.878	-0.0053	131	-0.0032	217
7,12-Dimethylbenz(a) anthracene	12	13	-0.0252	28	0.802	-0.0335	21	-0.0169	41
Benzo(b)fluoranthene	15	37	-0.0033	211	0.885	-0.0041	169	-0.0025	277
Benzo(a)pyrene	15	33	-0.0030	229	0.857	-0.0039	178	-0.0022	315
Dibenz(a,h)anthracene	15	14	-0.0017	420	0.568	-0.0026	267	-0.0007	990
Dibenzo(a,i)pyrene	15	12	-0.0030	232	0.838	-0.0039	178	-0.0021	330
Indeno(1,2,3-cd)pyrene	15	9	-0.0024	289	0.841	-0.0031	224	-0.0017	408

biological activity in the soil samples, these losses may be attributed to abiotic degradation. No significant degradation in poisoned soil was found for the other PAH compounds evaluated.

Generally, the degradation rates of PAH compounds in Kidman soils were not significantly different from those in McLaurin soils ($p < 0.05$).

Two PAHs, acenaphthylene and 3-methylcholanthrene, were included in the long-term degradation study but not in the short-term volatilization study. Apparent loss kinetics for these two compounds in Kidman and McLaurin soils are summarized in Table 17. The apparent loss of acenaphthylene was extensive.

There were no statistically significant differences in half-life values (Table 18) for acenaphthylene for $HgCl_2$ treated and untreated McLaurin soil. The similarities in $t_{1/2}$, with and without poisoning, may indicate that the presence of soil microbes did not influence the rate of loss of acenaphthylene from this unacclimated soil. Although the $t_{1/2}$ value for the poisoned Kidman soil (Table 18) was significantly different from the untreated soil, indicating some suppression of biodegradation, the addition of $HgCl_2$ to this soil did not greatly decrease the loss of acenaphthylene. At the end of the 65 day study, 96 percent of the chemical added was lost from the treated Kidman soil. Assuming acenaphthylene would behave similarly to naphthalene, abiotic loss should be relatively small. The extensive loss of acenaphthylene, even with the addition of $HgCl_2$, is likely due to volatilization. The Henry's law coefficient for acenaphthylene falls within the range $10^{<-5}<H<10^{-3}$ atm/mol/m^3 cited by Lyman et al. (1982) as a region for compounds of moderate volatility.

TABLE 16. DEGRADATION OF PAH COMPOUNDS IN KIDMAN AND McLAURIN SOILS POISONED BY 2 PERCENT $HgCl_2$

Compound	Percent degraded	
	Kidman	McLaurin
Naphthalene	12.0[a]	14.1[a]
1-Methylnaphthalene	12.3[a]	1.8[a]
Anthracene	8.7[a]	7.9[a]
Phenanthrene	17.4[a]	14.2[a]
Fluoranthene	0	3.1
Pyrene	4.4	5.5
Chrysene	5.9	3.2
Benz(a)anthracene	2.5	1.6
7,12-Dimethylbenz(a)anthracene	13.3	12.0
Benzo(b)fluoranthene	8.0	8.0
Dibenz(a,h)anthracene	13.8	6.4
Benzo(a)pyrene	7.3	8.3
Dibenzo(a,i)pyrene	10.3	9.3
Indeno(1,2,3-cd)pyrene	13.5	11.5

[a] Statistically significant ($p < 0.05$).

Negligible loss of 3-methylcholanthrene (3-MC) in the poisoned Kidman soil was observed, as the slope of the regression line was statistically equivalent to zero, indicated that biodegradation is the primary mechanism accomplishing destruction of this compound. As with 7,12-DMBA, 3-MC was less recalcitrant in Kidman soil than would be expected based upon molecular weight (high) and ring structure (large). However, the loss of 3-MC from McLaurin soil ($HgCl_2$ treated and untreated) was minimal over the 65 day study. The half-lives are extrapolations and serve to demonstrate the degree to which this compound tended to persist in soil. As with other large PAH compounds, volatile and abiotic loss of 3-MC are insignificant.

First-order plots of the data for loss of 3-MC from Kidman sandy loam soil in the absence and presence of $HgCl_2$ in Figures 5 and 6,

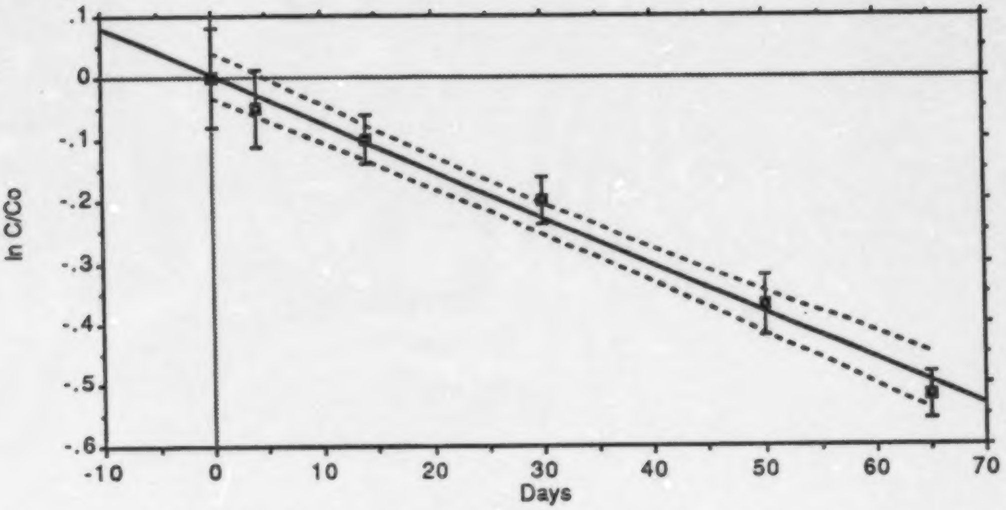


Figure 5. First order kinetic plots of the apparent loss of 3-methylcholanthrene from Kidman soil.

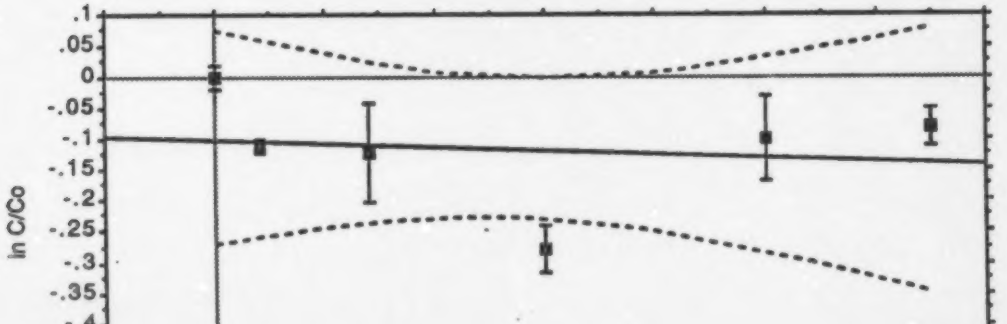


Figure 6. First order kinetic plots of the apparent loss of 3-methylcholanthrene from Kidman soil sterilized with $HgCl_2$.

TABLE 17. APPARENT LOSS KINETIC INFORMATION FOR PAH'S FROM KIDMAN AND MCLAURIN SOILS

						95% Confidence Interval			
						Lower limit		Upper limit	
Chemical	n	Co (mg/Kg)	k (day^{-1})	$t_{1/2}$ (days)	r^2	k (day^{-1})	$t_{1/2}$ (days)	k (day^{-1})	$t_{1/2}$ (days)
Kidman Soil									
Acenaphthylene	17	56.8	-0.134	5	0.876	-0.185	4	-0.084	8
3-methylcholanthrene	17	31.7	-0.0078	89	0.960	-0.0087	80	-0.0069	100
McLauren Soil									
Acenaphthylene	17	74.7	-0.039	18	0.708	-0.053	13	-0.025	28
3-methylcholanthrne	17	27.3	-0.0044	158	0.660	-0.0061	114	-0.0027	257

TABLE 18. APPARENT LOSS HALF-LIFE ($t_{1/2}$) OF ACENAPHTHYLENE AND 3-METHYLCHOLANTHRENE FROM KIDMAN AND MCLAURIN SOILS WITH AND WITHOUT ADDITION OF $HgCl_2$

	Kidman ($t_{1/2}$) (days)				McLaurin ($t_{1/2}$) (days)			
	Without $HgCl_2$		With $HgCl_2$		Without $HgCl_2$		With $HgCl_2$	
Compound	Average	95% Confidence Interval	Average	95% Confidence Interval	Average	95% Confidence Interval	Average	95% Confidence Interval
Acenaphthylene	5	4-8	17	12-32	18[a]	13-28	22[a]	15-41
3-methylcholanthrene	89	80-100	b		158[a]	114-257	238[a]	133-1216

[a] Slopes of the two lines for the same chemical (i.e., with and without $HgCl_2$) are not statistically different at 95% confidence level.

[b] Slope not statistically different from zero ($p<0.05$).

respectively. Standard deviations of triplicate samples for each point are indicated on each figure by brackets. Also, the dotted lines indicate the 95 percent confidence intervals about the slope of the line. First order plots of results similar to those shown in Figures 5 and 6 were generated for each chemical evaluated in this study.

Degradation of Pesticides

Toxaphene waste residue exhibited no measurable degradation after 150 days of incubation at an initial soil concentration of 20 mg/kg. The major mechanism for the degradation of toxaphene in soils occurs by reductive dechlorination (Parr and Smith 1976, Short 1986, Smith and Willis 1978). Fresh manure was applied to the soil waste mixture (2 percent manure, dry weight basis) to lower the redox potential of the soil. Application of manure was not effective in stimulating degradation of the toxaphene residue after the same period of incubation. Toxaphene would be classified as persistent in soil (Rao and Davidson 1981).

Degradation information for pesticides obtained in laboratory treatability studies using the Kidman and McLaurin soils is presented in Tables 19 and 20, respectively. Information obtained in the study included the initial soil concentration, degradation rate constant and constituent half-life based on a first-order kinetic rate model, and the coefficient of determination (r-squared value) for each constituent. The 95 percent confidence limits for the degradation rate constant and half-life value were also determined.

First order plots for heptachlor in Kidman sandy loam and McLaurin sandy loam soils are shown in Figures 7 and 8, respectively. Standard deviations of triplicate samples for each point are indicated in each

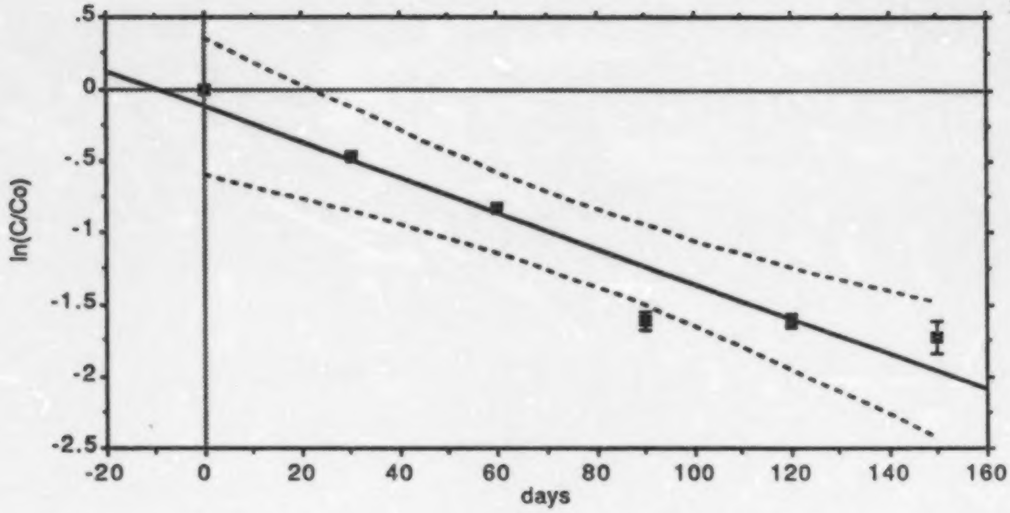


Figure 7. First order kinetic plots of the apparent loss of heptachlor from Kidman soil.

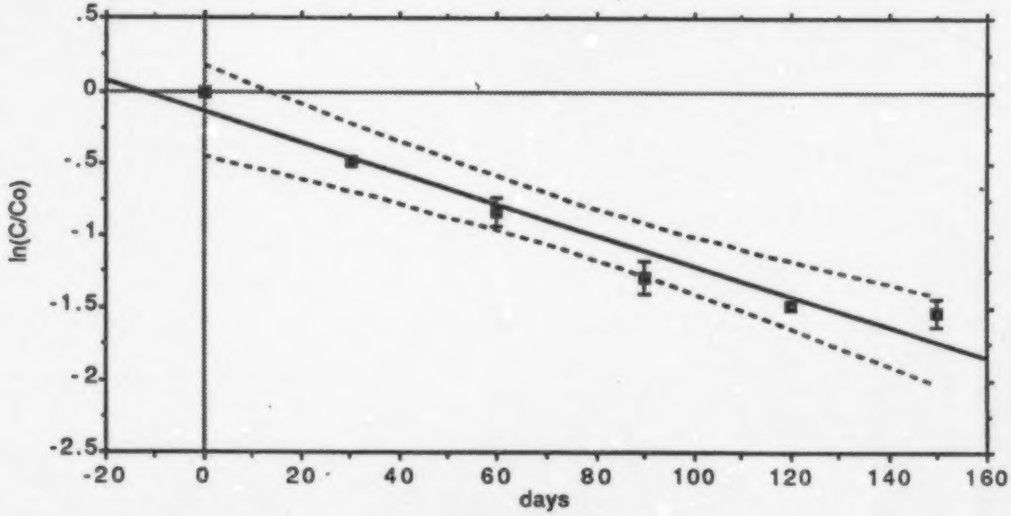


Figure 8. First order kinetic plots of the apparent loss of heptachlor from McLaurin soil.

figure by brackets. The dotted lines indicate the 95 percent confidence intervals about the slope of the line.

Very little information was available in the literature on degradation kinetics for warfarin, famphur, pronamide and dinoseb. Results of the degradation study for the other pesticides presented in Tables 19 and 20, are in agreement with published half-life values ($t_{1/2}$) for laboratory degradation studies conducted by other investigators (Rao and Davidson 1981). The $t_{1/2}$ values generated in the present study for lindane and DDT on the Kidman soil, however, were much shorter. Rao and Davidson (1981) reported values of 266 days for lindane and 1657 days for DDT, however, confidence intervals were not given. The pesticides investigated in this study exhibited half-life values between 17 and 385 days, and therefore would be classified as moderately persistent to persistent in soil (Rao and Davidson 1981).

The microbiological degradation of chlorinated pesticides has been reported to follow first-order kinetics (Hiltbold 1974, Nash and Woolson 1968). The first-order fit of the data generated in this study for many of the chlorinated pesticides was not as good as would be expected if the apparent loss truly followed first order kinetics. In many cases the plot of ln C/Co vs t displayed a curvelinear relationship. Other kinetic models should be investigated. Because multiple reactions, including volatilization, biodegradation, and abiotic degradation, are occurring simultaneously, the application of simple zero, first and second order kinetic equations may not adequately describe this system.

The degradation of organophosphorus pesticides could not be clearly characterized using a first-order reaction kinetic model. Use of first order kinetics overestimated half-lives for these pesticides. Saltzman et al. (1974) described the surface-catalyzed chemical degradation kinetics of parathion as two first-order reactions. Various mathematical expressions have been used to describe the degradation kinetics of the organophosphorus insecticides (Edwards 1972), including the approach of Saltzman et al. (1974) using multiple first order kinetic equations.

No loss of warfarin was observed in the Kidman soil. Negligible loss of warfarin and DDT in the McLaurin soil was indicated since the slope of the curves were statistically equivalent to zero. There was, however, an initial decrease in warfarin concentration in the McLaurin soil over the first five days of the study, after which no degradation occurred. Loss of aldicarb from Kidman soil was minimal over the 85 day study. The estimated half-live for aldicarb was obtained using an extrapolation method and serves only to indicate the persistence of this compound in Kidman soil.

The addition of $HgCl_2$ caused complete and immediate breakdown of the organophosphate pesticides including famphur and pronamide, as was evident from the extraction efficiency study, where less than 10 percent of the added pesticide was recovered at time zero. It appears that the presence of mercury catalyzed the breakdown of reactive side chains of these chemicals as discussed previously. Mercuric chloride, while providing excellent and continuous sterilization of soils, is not a useful soil sterilent for these chemically reactive compounds.

TABLE 19. APPARENT LOSS KINETIC INFORMATION FOR PESTICIDES FROM KIDMAN SOIL

						95% Confidence Interval			
						Lower limit		Upper limit	
Pesticide	n	Co (mg/Kg)	k (day^{-1})	$t_{1/2}$ (days)	r^2	k (day^{-1})	$t_{1/2}$ (days)	k (day^{-1})	$t_{1/2}$ (days)
Pentachloronitrobenzene	18	0.300	-0.0398	17	0.925	-0.046	15	-0.034	21
Disulfoton	18	1.56	-0.036	19	0.589	-0.052	13	-0.02	35
Methylparathion	18	1.04	-0.025	28	0.472	-0.039	18	-0.011	63
Phorate	17	1.42	-0.022	32	0.435	-0.036	19	-0.0082	85
Parathion	18	1.45	-0.017	41	0.690	-0.023	30	-0.011	63
Endosulfan	18	0.580	-0.016	43	0.854	-0.02	35	-0.013	53
Aldrin	18	0.429	-0.013	53	0.889	-0.016	43	-0.011	63
Famphur	22	82.7	-0.013	53	0.860	-0.015	46	-0.01	69
Heptachlor	18	0.588	-0.012	58	0.908	-0.014	50	-0.010	70
DDT	18	0.574	-0.015	60	0.524	-0.0173	40	-0.0057	122
Lindane	15	0.394	-0.0113	61	0.384	-0.0199	35	-0.0027	257
Pronamide	17	85.3	-0.0072	96	0.876	-0.0086	81	-0.0057	122
Dinoseb	17	103.1	-0.0067	103	0.890	-0.008	87	-0.0054	128
Aldicarb	22	99.1	-0.0018	385	0.435	-0.0027	257	-0.0008	845
Warfarin	22	117.8	0.0024[a]		0.520				

[a] Slope (k) of first order regression line is not significantly different from zero, no degradation observed.

TABLE 20. APPARENT LOSS KINETIC INFORMATION FOR PESTICIDES FROM MCLAURIN SOIL

						95% Confidence Interval			
						Lower limit		Upper limit	
Pesticide	n	Co (mg/Kg)	k (day^{-1})	$t_{1/2}$ (days)	r^2	k (day^{-1})	$t_{1/2}$ (days)	k (day^{-1})	$t_{1/2}$ (days)
Phorate	15	1.47	-0.029	24	0.812	-0.037	19	-0.02	
35									
Aldicarb	24	99.1	-0.023	30	0.921	-0.026	27	-0.02	35
Pentachloronitrobenzene	18	0.274	-0.0137	51	0.737	-0.0181	38	-0.0094	74
Lindane	15	0.340	-0.0106	65	0.436	-0.0178	39	-0.0034	204
Heptachlor	18	0.628	-0.011	63	0.933	-0.012	58	-0.0091	76
Famphur	24	98.9	-0.010	69	0.736	-0.012	58	-0.0071	98
Dinoseb	17	91.5	-0.0075	92	0.827	-0.0094	74	-0.0056	124
Pronamide	17	83.6	-0.0074	94	0.678	-0.01	69	-0.0046	151
DDT	18	0.452	-0.0025	a	0.184				
Warfarin	24	122.1	-0.0007	a	0.012				

[a] Slope (k) not statistically different from zero ($p<0.05$), no degradation observed.

In Table 21 the $t_{1/2}$ values for aldicarb, warfarin, lindane, and dinoseb in Kidman and McLaurin soils with and without the addition of $HgCl_2$ are presented. Figures 9 and 10 show first order plots for the loss of dinoseb from McLauren soil in the absence and presence of $HgCl_2$, respectively. Unlike PAH compound behavior, loss of these pesticides occurred in the presence of the sterilent.

There was no significant difference in $t_{1/2}$ values with and without the addition of $HgCl_2$ for the pesticide dinoseb in McLaurin soil and the pesticide lindane in both soils. This may indicate that the loss mechanisms for these compounds in the treated and untreated soil were the same, including abiotic degradation and/or volatilization.

The major mechanism for breakdown of chlorinated pesticides and dinoseb reported in the literature is microbial degradation (Kaufman 1974). In the unacclimated soils used in this study, however, microbial degradation may be limited. Mechanisms for abiotic loss of these compounds have not been extensively studied. Volatilization of chlorinated pesticides, however, has been observed in field and laboratory studies (Glotfelty et al. 1984; Harris and Lichtenstein 1961; Geobel et al. 1982), and may be the major loss mechanism of these pesticides in this study. The addition of $HgCl_2$ to dinoseb in the Kidman soil did affect the reaction kinetics significantly (Table 21) indicating that microbial degradation may have been a loss mechanism in this soil.

The loss of aldicarb in both soils and warfarin in McLaurin soil was accelerated by the addition of $HgCl_2$ (Table 21). Warfarin did not degrade (slope not statistically different from zero) in the McLaurin soil over the 88 day study. With the addition of $HgCl_2$, 72 percent of the warfarin was lost in this time period from McLaurin soil. The effect of $HgCl_2$ on

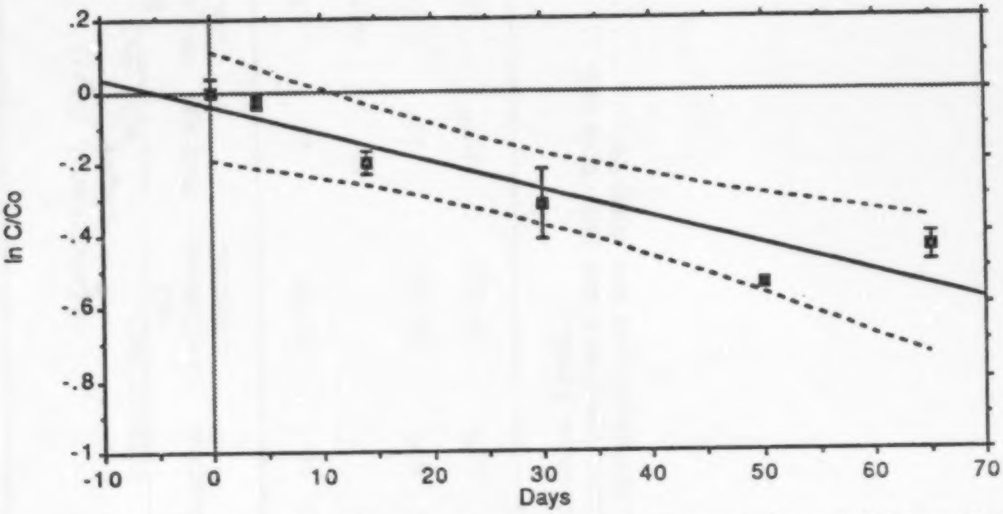


Figure 9. First order kinetic plots of the apparent loss of dinoseb from McLauren soil.

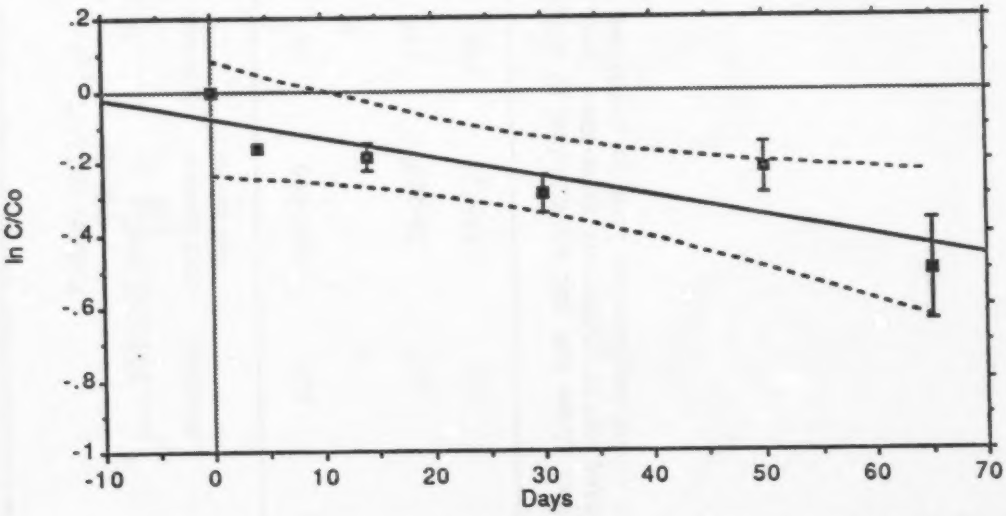


Figure 10. First order kinetic plots of the apparent loss of dinoseb from McLaurin soil sterilized with $HgCl_2$.

TABLE 21. APPARENT LOSS HALF-LIFE ($t_{1/2}$) FOR PESTICIDES FROM KIDMAN AND MCLAURIN SOILS WITH AND WITHOUT ADDITION OF $HgCl_2$

	Kidman soil ($t_{1/2}$) (days)				McLaurin soil ($t_{1/2}$) (days)			
	Without $HgCl_2$		With $HgCl_2$		Without $HgCl_2$		With $HgCl_2$	
Compound	Average	95% Confidence Interval	Average	95% Confidence Interval	Average	95% Confidence Interval	Average	95% Confidence Interval
Aldicarb	385	257-845	58	36-141	30	27-35	21	17-29
Warfarin	c		b				43	32-69
Lindane	61[a]	35-257	37[a]	27-60	65[a]	39-204	42[a]	27-91
Dinoseb	103	87-128	248	154-630	92[a]	74-124	122[a]	80-257

[a] Slope of the two lines are not statistically different at 95% confidence level.
[b] Slope not statistically different from zero ($p<0.05$), indicating that treatment was not observed.
[c] Slope of first order regression line is positive, indicating that treatment was not observed.

aldicarb was significant but not as dramatic in the McLaurin soil. In the Kidman soil the half-life decreased from 385 days to 58 days with the addition of $HgCl_2$. Similar to the organophosphate pesticides, aldicarb and warfarin contain reactive side chains. Mercury in $HgCl_2$ may be acting as a catalyst, accelerating the chemical breakdown of these compounds. The slope of the line for warfarin in the treated Kidman soil was not statistically significant ($p<0.05$).

Chlorinated Hydrocarbons and Aniline

Table 22 and 23 list the apparent loss rate constants and constituent half-lives based on a first order kinetic model for chlorinated hydrocarbons and aniline. Apparent compound loss rates for the highly volatile chlorinated hydrocarbons in the McLaurin soil were determined from methanol extracts of soils from the volatilization flasks obtained at various time intervals during the volatilization studeis, accounting for compound recovery efficiency from soil. Recovery efficiencies for 1,2,4-trichlorobenzene from McLaurin soil and hexachlorocyclopentidiene from both soils were poor (Table 23). All three compounds showed rapid disappearance from Kidman soil, and slower disappearance from the McLaurin soil.

First-order plots of the disappearance of 1,2,4-trichlorobenzene from McLaurin sandy loam soil in the absence and presence of $HgCl_2$ are shown in Figures 11 and 12 respectively.

The addition of $HgCl_2$ to either soil had no significant effect on the reaction kinetics of 1,2,4-trichlorobenzene, hexachlorocyclopentadiene, or 1,1,2-trichloroethane (Table 24). Similar $t_{1/2}$ values indicate nonbiologicalloss of these compounds primarily through volatilization.

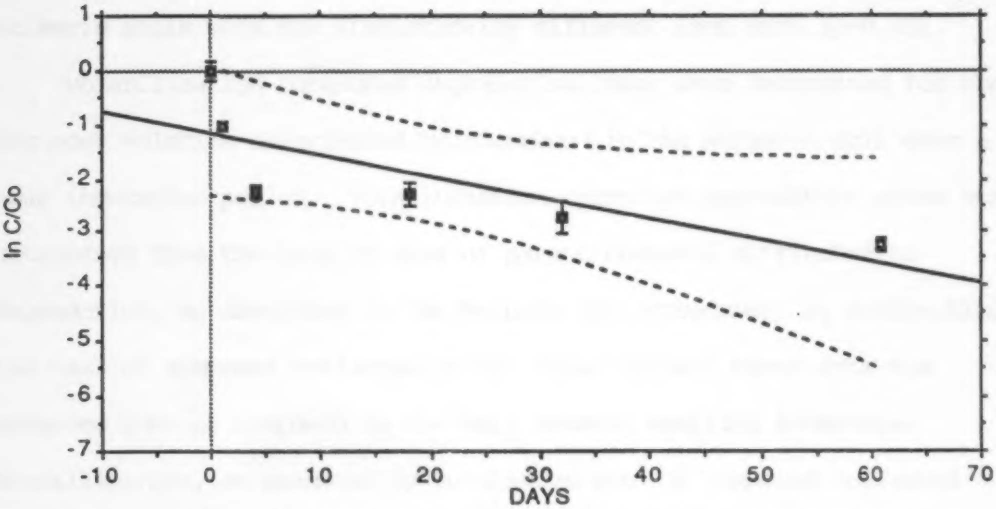


Figure 11. First order kinetic plots of the apparent loss of 1,2,4 trichlorobenzene from McLaurin soil.

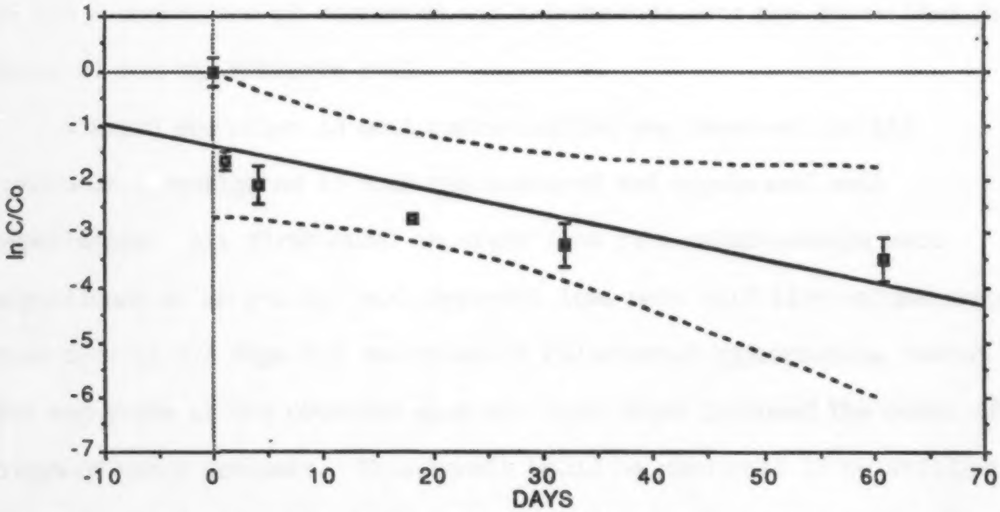


Figure 12. First order kinetic plots of the apparent loss of 1,2,4 trichlorobenzene from McLaurin soil sterilized with $HgCl_2$.

The slopes of the curves for aniline in the $HgCl_2$ treated Kidman and McLaurin soils were not statistically different from zero ($p=0.05$).

Volatilization corrected degradation rates were determined for the six most volatile chlorinated hydrocarbons in the McLaurin soil over a 50 hour incubation period. Volatilization corrected degradation rates were determined from the loss of mass of parent compound attributed to degradation, as described in the Methods and Procedures, by subtracting the mass of compound collected on the Tenax sorbent tubes from the observed loss of compound in the soil between sampling intervals. Volatilization, as measured by cumulative mass of compound collected on Tenax over the course of the experiments, was a significant loss mechanism for all compounds studied, ranging from 17 percent for 1,1,2,2-Tetrachloroethane, to over 76 percent for 1,1,2-Trichloroethane (Table 25). Volatilization corrected degradation results are presented in Table 26 and a comparison of corrected and uncorrected data are summarized in Table 27 for the McLaurin soil.

A rapid reduction in soil concentration was observed for all compounds investigated in both the poisoned and unpoisoned soil experiments. All first order apparent loss rate relationships were significant at an $p=0.05$, with apparent loss mean half life values ranging from 0.07 to 0.6 days for the volatile chlorinated hydrocarbons tested. The magnitude of the observed apparent loss rates followed the order of compound vapor pressure. This result would be predicted if volatilization was the primary loss mechanism from soil systems. Apparent loss rate values from low to high followed the order: Aniline = 1,2,4-Trichlorobenzene < Hexachlorocyclopentadiene < Chloromethylmethyl ether =

TABLE 22. APPARENT LOSS KINETICS USING FIRST ORDER KINETICS MODEL FOR CHLORINATED HYDROCARBONS AND ANILINE IN KIDMAN SOIL WITHOUT ADDITION OF $HgCl_2$

						95% Confidence Interval			
						Lower limit		Upper limit	
Compound	n	Co (mg/Kg)	k (day^{-1})	$t_{1/2}$ (days)	r^2	k (day^{-1})	$t_{1/2}$ (days)	k (day^{-1})	$t_{1/2}$ (days)
Aniline	22	20.7	-0.072	10	0.882	-0.086	8	-0.057	12
1,2,4-trichlorobenzene	18	0.904	-0.093	7	0.692	-0.126	6	-0.060	12
Hexachlorocyclopentadiene	15	0.051	-0.256	3	0.709	-0.355	2	-0.158	4

TABLE 23. APPARENT LOSS KINETICS USING FIRST ORDER KINETICS MODEL FOR CHLORINATED HYDROCARBONS AND ANILINE IN MCLAURIN SOIL WITHOUT ADDITION OF $HgCl_2$

						95% Confidence Interval			
						Lower limit		Upper limit	
Compound	n	Co (mg/Kg)	k (day^{-1})	$t_{1/2}$ (days)	r^2	k (day^{-1})	$t_{1/2}$ (days)	k (day^{-1})	$t_{1/2}$ (days)
Aniline	24	23.0	−0.025	28	0.521	−0.036	19	−0.015	46
1,2,4-trichloro-benzene	18	0.292	−0.040	17	0.623	−0.057	12	−0.024	29
Hexachlorocyclopenta-diene	15	0.038	−0.173	4	0.725	−0.237	3	−0.109	6
1,1-Dichloroethylene	5	156.6	-10.49	0.07	0.994	-11.98	0.06	-9	0.08
1,1,1-Trichloroethane	6	155.2	-4.56	0.15	0.928	-6.34	0.11	-2.78	0.25
1,1,2-Trichloroethane	7	155	-1.70	0.41	0.875	-2.45	0.28	-0.96	0.72
1,1,2,2-Tetrchloroethane	7	157	-1.82	0.38	0.943	-2.33	0.30	-1.30	0.53

TABLE 24. APPARENT LOSS HALF-LIFE ($t_{1/2}$) FOR 1,2,4-TRICHLOROGENZENE, HEXACHLOROCYCLOPENTADIENE AND ANALINE IN KIDMAN AND MCLAURIN SOILS WITH AND WITHOUT ADDITION OF $HgCl_2$

	Kidman ($t_{1/2}$) (days)						McLaurin ($t_{1/2}$) (days)	
	Without $HgCl_2$		With $HgCl_2$		Without $HgCl_2$		With $HgCl_2$	
Compound Interval	Average	95% Confidence Interval	Average	95% Confdence Interval	Average	95% Confidence Interval	Average	95% Confidence
Aniline	10	8-12	[a]	-	28	19-46	[a]	-
1,2,4-trichloro-benzene	7	6-12	9	6-15	17	12-29	16	10-39
Hexachlorocyclo-pentadiene	3	2-4	4	2-18	4	3-6	4	3-8
1,1-Dichloroethylene					0.07	0.06-0.08		
1,1,1-Trichloroethane					0.15	0.11-0.25		
1,1,2,2-Tetra-chloroethane					0.38	0.30-0.53		
Chloromethyl-methyl ether							0.25	0.17-0.54
1,1,2-Trichloroethane					0.41	0.28-0.72	0.32	0.23-0.53
1,2-Dibromo-3-chloropropane							0.60	0.40-1.26

[a] no statistical significance of slope ($p<0.05$).

TABLE 25. VOLATILIZATION OF CHLORINATED HYDROCARBONS FROM MCLAURIN SOIL

Compound	Percent Volatilized No $HgCl_2$	With $HgCl_2$
1,1,Dichloroethylene	16.9	-
1,1,1-Trichloroethane	64.6	-
1,1,2-Trichloroethane	60.8	76.4
1,1,2,2-Tetrachloroethane	36.8	-
Chloromethylmethyl ether	-	60.1
1,2,Dibrom0-3-chloropropane	< [illegible]	63.5

TABLE 26. VOLATILIZATION CORRECTED DEGRADATION KINETIC INFORMATION FOR CHLORINATED COMPOUNDS APPLIED TO MCLAURIN SANDY LOAM AT -0.33 BAR COIL MOISTURE CONTENT.

						95% Confidence Interval			
						Lower limit		Upper limit	
Compound	n	Co (mg/Kg)	k (day^{-1})	$t_{1/2}$ (days)	r^2	k (day^{-1})	$t_{1/2}$ (days)	k (day^{-1})	$t_{1/2}$ (days)
Degradation Data Corrected for Volatilization, Unpoisoned Soil									
1,1,Dichloroethylene	4	156.0	-16.34	0.04	0.788	-42.14	0.02	-	-
1,1,1-Trichloroethane	4	155.2	-9.60	0.07	0.936	-17.21	0.04	1.97	0.35
1,1,2-Trichloroethane	6	155	-30.55	0.02	0.599	-65.28	0.01	-	-
1,1,2,2-Tetrchloroethane	6	147	-53.42	0.01	0.588	-115.54	0.01	-	-
Degradation Data Corrected for Volatilization, HgCl Poisoned Soil									
Chloromethylmethyl ether	5	123.6	-55.68	0.01	0.558	-146.69	0.00	-	-
1,1,2-Trichloroethane	5	155	-63.48	0.02	0.536	-172.10	0.00	-	-
1,2-Dibromo-3-chloropropane	6	144.9	-70.34	0.01	0.516	-164.05	0.00	-	-

[a] degradation rate not statistically different from zero

TABLE 27. COMPARISON OF VOLATILIZATION CORRECTED AND UNCORRECTED DEGRADATION KINETIC DATA FOR CHLORINATED HYDROCARBONS IN MCLAURIN SOIL.

Compound	McLaurin ($t_{1/2}$)			
	Volatilization Corrected		Volatilization Uncorrected	
	Average	95% Confidence	Average	95% Confidence
1,1-Dichloroethylene	0.04	NSD[a]	0.07	0.06–0.08
1,1,1-Trichloroethane	0.07	0.04–0.35	0.15	0.11–0.25
1,1,2,2-Tetrachloroethane	0.01	NSD[a]	0.38	0.30–0.53
Chloromethylmethyl ether	0.01	NSD[a]	0.25	0.17–0.54
1,1,2-Trichloroethane	0.02	NSD[a]	0.32	0.23–0.53
1,2-Dibromo-3-chloropropane	0.01	NSD[a]	0.60	0.40–1.26

[a] no statistical difference in degradation

1,1,2,2-Tetrachloroethane = 1,1,2-Trichloroethane = 1,2-Dibromo-3-chloropropane = 1,1,1-Trichloroethane < 1,1,Dichloroethylene. Based on results shown in Tables 26 and 27 for the unpoisoned McLaurin soil, observed loss of all constituents except 1,1,1-Trichloroethane could not be attributed statistically to biodegradation. Only 1,1,1-Trichloroethane exhibited a volatilization corrected degradation rate that was significantly greater than zero at $p=0.05$. The corrected degradation rate constant in McLaurin soil of 9.60 + 7.63 d^{-1}, corresponding to a mean corrected half life of 0.07 days for 1,1,1-Trichloroethane (range 0.04 to 0.35 days), was not significantly different ($p=0.05$) from the uncorrected rate value.

Abiotic degradation studies conducted for the volatile chlorinated hydrocarbons confirmed the significance of volatilization as a loss mechanism for this class of compounds. All abiotic, uncorrected loss rates were significantly greater than zero, while all volatilization corrected rates were not different from zero at $p=0.05$. There was no significant difference ($p=0.05$) between sterilized and unsterilized apparent loss rates for 1,1,2-Trichloroethane. In addition, total 1,1,2-Trichloroethane mass emitted (Table 25) indicated only a 20 percent increase in volatilization in sterilized soil suggesting that loss from McLaurin soil is not significantly affected by soil biological activity.

PARTITION COEFFICIENTS FOR SUBSTANCES IN SOIL

SAR-derived partition coefficients for both experimental soils for the chemicals in the four classes evaluated are summarized in Tables 28-31. Values for aqueous-soil (K_d), aqueous-oil (K_o), and aqueous-air (K_h) partition coefficients are presented in Tables 28-30. As expected, PAH and pesticide compound exhibited high K_o and K_d values, while the volatile class compounds showed high K_h values. Partition coefficients estimated using SARs were in good agreement with literature values for coefficients for the compounds addressed. Values for aqueous-soil (Kd) partition coefficients based on first order molecular connectivity index (MCI) calcuations are presented in Table 31.

Apparent Loss of Tetraalkyllead (TAL)

Tetraalkyllead (TAL) mixture typically consists of tetraethyllead (TEL), tetramethyllead (TML), triethylmethyllead (TEML), and trimethylethyllead (TMEL). GC/MS analysis indicated that the sample used contained TEL, TEML, and a triethyllead alcohol.

The degradation of TAL is thought to follow the reaction sequence shown below:

$$R_4Pb\text{-->}R_3Pb^{+}\text{-->}R_aPb^{2+}\text{-->}Pb^{2+} \qquad (1)$$

where R - Me, Et or Me-Et combination. Tetraalkyllead degrades into alkyllead salts and inorganic lead.

All species of lead likely to be present in this study are adsorbed by organic matter, silica, road dust, sediments, and/or soils (Harrison and Laxan 1978, Jarvie et al. 1981, van Cleavenberger 1986, Blais and Marshall 1986). Sorption of TAL by road dust and atmospheric particles is usually followed by rapid decomposition to trialkyllead salts (Harrison and Laxan 1978, Jarvie et al. 1981).

Lead in soil extracts and in air samples (volatilized lead) for this study were determined using an atomic adsorption spectrophotometer (AAS). AAS analysis for total lead in solution cannot be used to distinguish lead species present in soil or air fractions. Volatilization of lead was

TABLE 28. CALCULATED SOIL/WATER (Kd), OIL/WATER (Ko), AND AIR/WATER (Kh) PARTITION COEFFICIENTS FOR 16 PAH COMPOUNDS.

Compound	log Kd (McLaurin)	log Kd (Kidman)	log Ko	Log Kh
Acenaphthylene	1.72	1.38	4.23	-1.22
Benz(a)anthracene	3.24	2.90	5.95	-5.36
Benzo(a)pyrene	3.67	3.33	6.43	-2.75
Chrysene	3.24	2.90	5.95	-2.41
Dibenzo(a,h)anthracene	3.60	3.26	6.35	-5.52
Ideno(1,2,3-cd)pyrene	5.27	4.93	8.24	-7.62
3-Methylcholanthrene	4.73	4.38	7.63	-
Fluoranthene	2.97	2.62	5.64	-3.60
1-Methylnapthalene	1.52	1.18	4.00	-
Naphthalene	1.01	0.67	3.42	-1.97
Phenanthrene	2.11	1.76	4.66	-2.30
Pyrene	2.96	2.61	5.63	-4.27
Benzo(b)fluoranthene	4.19	3.86	7.02	-2.91
7,12-Dimethylbenz(a)anthracene	3.61	3.27	6.36	-
Anthracene	2.10	1.75	4.65	-1.59
Benz(c)acridine	-	-	-	-

TABLE 29. CALCULATED SOIL/WATER (Kd), OIL/WATER (Ko), AIR/WATER (Kh) PARTITION COEFFICIENTS FOR 22 PESTICIDES.

Compound	log Kd (McLaurin)	log Kd (Kidman)	log Ko	Log Kh
Aldrin	0.65	0.31	0.62	-1.93
Cacodylic Acid	-2.31	-2.65	-0.32	-
Chlordane, technical	0.44	0.10	2.79	-2.40
DDT	1.14	0.79	3.57	-2.44
Dieldrin	0.56	0.22	2.92	-4.69
Dinoseb	-	-	2.25	-
Disulfoton	-2.31	-2.65	-0.32	-4.13
Endosulfan	1.21	0.86	3.65	-2.44
Famphur	-	-	-	-
Heptachlor	1.55	1.21	4.04	-0.97
Alpha Lindane	1.46	1.12	3.94	-4.47
Methyl parathion	0.65	0.31	3.02	-5.56
Parathion	1.06	0.72	3.48	-4.04
Phorate	0.58	0.24	2.94	-3.40
Pronamide	-	-	-	-
Toxaphene	0.96	0.62	3.37	-5.13
Warfarin	0.19	-0.15	2.49	-
Aldicarb	-1.61	-1.95	0.46	-6.59
Pentachloronitrobenzene	-	-	-	-
Diethyl-p-nitrophenyl phosphate	-	-	-	-
Floracetic acid	-	-	-	-
Formaldehyde	-	-	-	-

TABLE 30. CALCULATED SOIL/WATER (Kd), OIL/WATER (Ko), AND AIR/WATER (Kh) PARTITION COEFFICIENTS FOR 13 CHLORINATED HYDROCARBONS.

Compound	log Kd (McLaurin)	log Kd (Kidman)	log Ko	Log Kh
Bis-(chloromethyl) ether	-2.68	-3.02	-0.75	-
Chloromethyl methyl ether	-1.41	-1.75	0.69	-
1,2-Dibromo-3-chloropropane Dichlorodifluoromethane	-0.17	-0.51	2.09	2.01
1,1-Dichloroethylene 1,1,1-Trichloroethane	0.13	0.47	2.14	-0.79
1,1,2,2-Tetrachloroethane	2.63	2.29	5.26	-1.81
1,1,2-Trichloroethane	-0.16	-0.50	2.10	-1.51
1,2,2-Trichlorotrifluoroethane	-0.66	-1.01	1.53	-
Trichloromonofluoroethane	-	-	-	-
Hexachlorocycopentadiene	2.68	2.34	5.31	-1.37
4,4-Methylene-bis-(2-chloroaniline)	0.96	0.62	3.37	-
1,2,4-Trichlorobenzene	1.63	1.29	4.13	-0.77

TABLE 31. LOG Kd VALUES ESTIMATED USING FIRST ORDER MCIS.

Compound	MCI‡	log Koc*	log Kd (McLaurin)	log Kd (Kidman)
PNAs				
Acenaphthylene	5.949	3.69	3.99	3.65
Benz(a)anthracene	8.916	5.27	6.96	6.62
Benzo(a)pyrene	9.916	5.80	7.96	7.62
Chrysene	8.933	5.27	6.97	6.63
Dibenzo(a,h)anthracene	10.865	6.30	8.91	8.56
Indeno(1,2,3-cd)pyrene	10.916	6.33	8.96	8.62
3-Methylcholanthrene	10.327	6.01	8.37	8.03
Fluoranthene	7.949	4.75	5.99	5.65
1-methylnaphthalene	5.377	3.39	3.42	3.08
Naphthalene	4.966	3.17	3.01	2.67
Phenanthrene	6.949	4.22	4.99	4.65
Pyrene	7.933	4.74	5.97	5.63
Benzo(b)fluoranthene	9.933	5.80	7.97	7.63
7,12-dimethylbenzanthracene	9.771	5.72	7.81	7.47
anthracene	6.933	4.21	4.97	4.63
Benz(c)acridine	8.899	5.26	6.94	6.60
Pesticides				
Aldrin	9.254	5.44	7.30	6.95
Cacodylic Acid	2.000	1.60	0.04	-0.30
Chlordane	8.114	4.84	6.16	5.81
DDT	8.876	5.24	6.92	6.58
Dieldrin	9.714	5.69	7.76	7.41
Dinoseb (2,4 dinitro-6-sec-butylphenol)	7.879	4.72	5.92	5.58
Disulfoton	6.682	4.08	4.72	4.38
Endosulfan	7.942	4.75	5.98	5.64
Famphur	8.987	5.30	7.03	6.69
Heptachlor	7.703	4.62	5.74	5.40
Lindane (hexachlorocyclohexane) tech	5.464	3.44	3.51	3.16
alpha	5.464	3.44	3.51	3.16
Methyl parathion	7.504	4.52	5.55	5.20
Parathion	8.504	5.05	6.55	6.20
Phorate	6.182	3.82	4.22	3.88
Pronamide	6.777	4.13	4.82	4.48
Toxaphene	8.225	4.90	6.27	5.92
Warfarin	11.075	6.41	9.12	8.77
Aldicarb	5.621	3.52	3.66	3.32
pentachloronitrobenzene	6.375	3.92	4.42	4.07
Diethyl-p-nitrophenyl phosphate	8.504	5.05	6.55	6.20
Floracetic acid	2.808	2.03	0.85	0.51
Formaldehyde	1.000	1.07	-0.96	-1.30
Chlorinated Hydrocarbons				
Bis-(chloromethyl) ether	2.414	1.82	0.46	0.11
Chloromethyl methyl ether	1.914	1.55	-0.05	-0.39
1,2-Dibromo-3-chloropropane	2.808	2.03	0.85	0.51
Dichlorodifluoromethane	2.000	1.60	0.04	-0.30
1,1-Dichloroethylene	1.732	1.46	-0.23	-0.57
1,1,1-Trichloroethane	2.000	1.60	0.04	-0.30
1,1,2,2-Tetrachloroethane	2.643	1.94	0.68	0.34
1,1,2-Trichloroethane	2.270	1.74	0.31	-0.03
1,1,2-Trichlorotrifluoroethane	3.250	2.26	1.29	0.95
Trichloromonofluoroethane	2.561	1.90	0.60	0.26
Hexachlorocycopentadiene	4.887	3.13	2.93	2.59
4,4-Methylene-bis-(2-chloroaniline)	8.059	4.81	6.10	5.76
1,2,4-trichlorobenzene	4.198	2.76	2.24	1.90
Misc. Compounds				
Aniline	3.394	2.34	1.44	1.09
Mitomycin C	10.913	6.32	8.95	8.61
Pyridine	3.000	2.13	1.04	0.70
Tetraethyl Lead	4.243	2.79	2.28	1.94
Uracil mustard	6.774	4.13	4.82	4.47

‡First order molecular connectivity index

*Calculated from first order MCI using regression equation (11) developed by Sagljic (1987).

evaluated, however, degradation could not be determined for TAL since the AAS method cannot distinguish between TAL and lead in breakdown products.

Two extraction procedures were used to remove lead species including TAL, TAL salts, and Pb^{2+} from the soil. At each sampling interval a subsample of soil was either (1) extracted with methylisobutal-ketone (MIBK) or (2) digested with hot nitric acid-hydrogen peroxide (Method 3050 U.S. EPA 1982). Volatilized TAL (sorbed by Tenax traps) was extracted with MIBK. Since specific organic lead species extracted with MIBK is unknown, the use of MIBK as a solvent did not facilitate isolation of various organic and inorganic forms of lead. Nonextractable lead, defined as the difference between lead in the hot nitric acid digestion and the MIBK extraction, may be inorganic and organic lead species sorbed to soil or various lead spoecies not as readily extracted with MIBK.

Table 32 shows the distribution of lead as volatile, organic (MIBK) extractable and nonextractable with time. Less than 10 percent of the total lead added to Kidman soil volatilzed over the first four hours of the study. After 24 hours 49.4 percent of the total lead had volatilized. The ratio of MIBK extractable and nonextractable lead over this time period was relatively constant, indicating a loss of lead from both fractions. Either volatilization of lead was from both fractions, or volatilization was occurring from one fraction with the desorption and/or decomposition of lead in the other fraction replacing that lost through volatilization.

The TAL parent compounds and trialkyllead salts are volatile and are soluble in MIBK, whereas the dialkyllead salts and inorganic lead are less volatile and are more polar in nature. No conclusion, however, can be

TABLE 32. MASS BALANCE FOR TETRAALKYL LEAD IN A SOIL SYSTEM

Time (hr)	n	Hot[1] Nitric Acid Soluble Lead % Total	Organic[2] Extractable (MIBK) Lead % Total	Nonextractable[3] Lead % Total	Volatile[4] Loss % Total	Mass Balance Total Lead[5] Acid Extract + Volatile mg/kg
0	2	99.6	57.2	42.4	0.4	71.7
1	2	98.3	56.4	41.9	1.8	71.8
2	2	96.7	59.8	36.9	3.4	72.1
4	2	92.7	52.5	40.2	7.2	71.4
8	2	83.5	50.6	32.8	16.5	70.3
24	2	50.5	33.2	17.3	49.4	64.8
70	2	25.9	5.0	21.0	74.0	68.6

[1] hot nitric acid soluble lead was measured experimentally.

[2] organic extractable lead was measured experimentally.

[3] nonextractable lead was calculated as the difference between hot nitric acid soluble lead and organic extractable lead.

[4] volatile loss of lead was measured independently of other measurements.

[5] the mass balance was calculated as mg/kg as follows:
hot nitric acid lead(1) + volatile loss(4) = total lead.

made concerning specific mechanisms of reactions in this system. After 70 hours, 74 percent of the added lead was volatilized. The majority of the lead remaining in the soil (81 percent) was in the nonextractable form.

LAND TREATMENT MODEL APPLICATIONS

The mathematical models (RITZ and VIP) were used to simulate the behavior of eight pesticides in Kidman soil at a time period beyond the laboratory determined half-life. Input parameters for the models included: pesticide concentration in soil (g/m^3), soil water content corresponding to 90 percent saturation (θ = 22 percent), calculated partition coefficients (Kh and Kd), Kidman soil parameters, and laboratory determined kinetic (k) values. Table 33 lists the predicted concentration of each pesticide in soil water, soil air, and soil solid phase after 91 days at the bottom of the zone of pesticide incorporation (15 cm), in an HWLT unit. The concentration of the pesticides in soil water, soil air, and soil solid phases at the next depth increment, 18 cm, were at least six orders of magnitude less than at 15 cm and were below analytical detection limits. The organophosphorus pesticides were predicted to degrade significantly in 91 days (96.2 percent for disulfoton to 78.8 percent for parathion). Approximately 70 percent of the applied chlorinated pesticides were predicted to degrade in this time period.

When apparent loss was eliminated in the models (by setting k=0), treatment was limited to the sorptive capacity (immobilization) of the soil for each pesticide. No movement through volatilization or leaching was predicted by the models except for toxaphene where detectable concentrations were predicted to be volatilized and to leach from the zone of incorporation in 91 days. Therefore, from the time of application to

TABLE 33. CONCENTRATIONS OF PESTICIDES IN SOIL WATER, SOIL AIR, AND SOIL SOLID PHASES AND PERCENT DECAY AT 15 cm DEPTH AFTER 81 DAYS AS PREDICTED BY THE MATHEMATICAL MODELS.

	Concentration in soil water (g/m^3)	Concentration in soil air (g/m^3)	Concentration in soil solid phase (g/m^3)	% decay
Disulfoton	2×10^{-5}	2×10^{-9}	6×10^{-8}	96
Phorate	5×10^{-6}	1×10^{-9}	2×10^{-7}	87
Methylparathion	5×10^{-7}	1×10^{-12}	1×10^{-7}	90
Parathion	2×10^{-8}	5×10^{-13}	3×10^{-7}	79
Aldrin	1×10^{-10}	2×10^{-12}	1×10^{-7}	69
Endosulfan	2×10^{-8}	7×10^{-11}	2×10^{-7}	72
Heptachlor	1×10^{-8}	1×10^{-9}	2×10^{-7}	66
Toxaphene	1×10^{-5}	2×10^{-4}	2×10^{-5}	0

91 days, significant treatment was observed in the modeled systems (with and without degradation as an input parameter), with no migration of the pesticides out of the zone of incorporation (15 cm) at the soil concentrations and soil water content of 22 percent.

The prediction of no leaching observed by both models under conditions used in the laboratory study is supported by both laboratory and field studies of other investigators. Only trace amounts of chlorinated pesticides have been found below the zone of incorporation in field studies after long time periods (Freeman et al., 1975, Lichtenstein et al., 1971, Nash and Woolson, 1967, Rao and Murty, 1980). Although organophosphorus pesticides are relatively soluble compared with chlorinated pesticides, they also do not readily migrate in soil systems (Singh and Singh, 1984, Voerman and Besemer, 1970, Weber, 1972).

For losses due to volatilization, the VIP model employs a partition coefficient between water and air and a diffusion gradient through the soil-pore air space. The model predicted no significant diffusion of any of the pesticides with the exception of toxaphene, into the atmosphere under conditions used in this study. Volatilization of chlorinated and organophosphorus pesticides, however, has been observed in field studies (Burt et al., 1965, Glotfelty et al., 1984, Grenney et al., 1987, Harris & Chapman, 1980, Harris and Lichtenstein, 1961, Nash, 1983). Maximum loss due to volatilization generally occurred within the first few days after application. Field studies are often performed without making efforts to minimize potential volatile losses. Factors influencing volatilization include the concentration of the pesticide used, soil/pesticide sorption reactions, soil temperature, soil water content, application method, relative humidity of the air and rate of movement of air over the soil surface (Farmer et al., 1972, Harris and Lichtenstein, 1961, Igue et al., 1972, Spencer and Cliath, 1977). In the laboratory study reported here, methods were used to minimize volatilization as described previously. Methods for minimizing volatile losses with field application of pesticides are given by the U.S. EPA (U.S. EPA, 1984a and b).

Since the VIP and RITZ models do not presently address non-steady state flow or macropore flow, fracture flow or immiscible flow, the intended application, at present, is primarily to aid in environmental pathways analysis, i.e., to indicate the results of the interactions of natural processes (degradation and immobilization) on the relative distribution of multiple chemicals in soil/waste systems.

The use of the VIP model for evaluating the mobility of polynuclear aromatic hydrocarbons (PAH compounds) under steady state conditions in laboratory column reactors, conducted as part of this research project, is discussed in detail by Grenney et al. (1987).

TRANSFORMATION STUDIES

The distribution of ^{14}C from the incubation of $(12-^{14}C)$DMBA with McLaurin sandy loam soil is summarized in Table 34. Total ^{14}C recoveries varied from 78 to 90% over the 28-day incubation period for both nonpoisoned and poisoned (2% $HgCl_2$) samples. The recovery efficiencies range is typical for a ^{14}C tracer study (Bulman et al. 1985).

Parent ^{14}C DMBA was extensively biodegraded with a half life of 17 days. Microbial transformation half-life was determined from the decrease of the DMBA ^{14}C fraction over time, which was corrected for abiotic loss and volatilization. These results are consistent with the results obtained for the nonradiolabeled DMBA degradation study, which showed biodegradation half lives of 20 to 28 days (Park 1987). Abiotic loss of ^{14}C DMBA from soil samples poisoned by 2% $HgCl_2$ was statistically not significant ($p=0.05$). ^{14}C DMBA volatilization was not detected during the 28-day soil incubation period.

Table 34 also shows that the decrease in the parent PAH ^{14}C is accompanied by an increase in metabolite ^{14}C fraction. Incorporation of ^{14}C DMBA into a nonextractable soil residue ^{14}C increased from 12 to 17%, however, the increase was not statistically significant ($p=0.05$). Evolution of $^{14}CO_2$ was not detected during the 28 days of incubation.

These results do not demonstrate that the parent compound was not metabolized to CO_2 since ^{14}C DMBA used was radiolabeled only at the 12 position carbon. In order to detect $^{14}CO_2$ the benzene ring which contained the carbon-12 was required to be mineralized to CO_2.

The HPLC chromatogram of DMBA metabolites is presented in Figure 13. The chromatogram revealed several metabolic products. Peaks 7, 8, and 9 were tentatively characterized as 10-hydroxy-, 4-hydroxy-, and 5-hydroxy-DMBA, respectively. HPLC retention time of these metabolites were identical with those given by reference standards. The mass spectrum of peak 3 displayed ions at m/e values of 272 (molecular ion), 257 (loss of CH_3), and 226 (loss of CH_3, OH, and CH_2) and indicated that the metabolite is 7,12-dihydro-12-methyl-7-methylene-benz(a)anthracene-12-ol. HPLC elution profile (Figure 14) from the incubation of ^{14}C DMBA revealed a complex mixture of metabolic products which was similar to the HPLC chromatogram (Figure 13) for nonradiolabeled PAH metabolites. The elution profile further shows the formation of highly polar metabolic products eluting prior to HPLC retention time of 15 min.

Results for Ames assay testing with strain TA-100 for DMBA metabolites at low and neutral pH soil are presented in Figures 15 and 16, respectively. The highly polar metabolic fraction (HPLC retention time 0-15 min) was mutagenically inactive towards TA-100 for both soil pH conditions, suggesting that these metabolites may be the detoxified conjugation products of soil microbial enzymes. Cerniglia and Gibson (1979), who studied the oxidation of ^{14}C benzo(a)pyrene by Cunninghamella elegans, demonstrated that the metabolites eluting in the very polar HPLC region were mostly sulfate conjugates of dihydroxy benzo(a)pyrene metabolites and benzo(a)pyrene phenols.

TABLE 34. TRANSFORMATIONS OF (^{14}C) 7,12-DIMETHYLBENZ(A)ANTHRACENE BY MCLAURIN SANDY LOAM SOIL[a].

Time (days)	^{14}C appearing in each fraction (%)				
	Soil Extract		Soil Residue	CO_2	Total
	7,12-dimethylbenz(a)-anthracene (parent compound)	Metabolites			
0	62 (69)	4 (6)	12 (13)	0 (0)	78 (88)
14	26	43	16	0	85
28	20 (60)	53 (11)	17 (16)	0 (0)	90 (87)

[a] Poisoned (control) data in parentheses.

Moderate and nonpolar (HPLC retention time 15-33 min and 35-45 min, respectively) metabolite fractions induced a positive response (mutagenic ratio greater than 2.5 (U.S. EPA 1983b)) for both soils. The mutagenic potential of these metabolite fractions, however, decreased during the 28 day soil incubation time. This detoxication potential of DMBA may be important for engineering management and control of hazardous wastes containing this PAH compound since toxicity reduction as a function of incubation time in the soil can be used to assess the success of treatment. The phenomenon of detoxification was reported by other investigators (Sims 1982, Sims et al. 1986) who found that the mutagenicity of polar transformation products of benzo(a)-pyrene increased and then decreased with incubation time, or treatment time, in the soil.

Mutagenic responses for the metabolites formed from low and neutral pH soil were not different. Soil pH adjustment changed the microbial populations by one order of magnitude, but significant and equivalent amounts of both bacteria and fungi still existed in both soils after 30 days incubation (Table 35). Thus, differences in the metabolic products between low and neutral pH soil are not likely, and similar mutagenic responses between two soil treatments may have resulted.

Parent ^{14}C DMBA biodegraded extensively with a half life of 17 days. The decrease in the parent ^{14}C PAH (62% to 20%) was accompanied by an increase in metabolite ^{14}C fraction (4% to 53%). Soil residue ^{14}C, however, did not increase significantly ($p=0.05$) during the 28 days of soil incubation. DMBA was transformed into several metabolic products in the McLaurin soil.

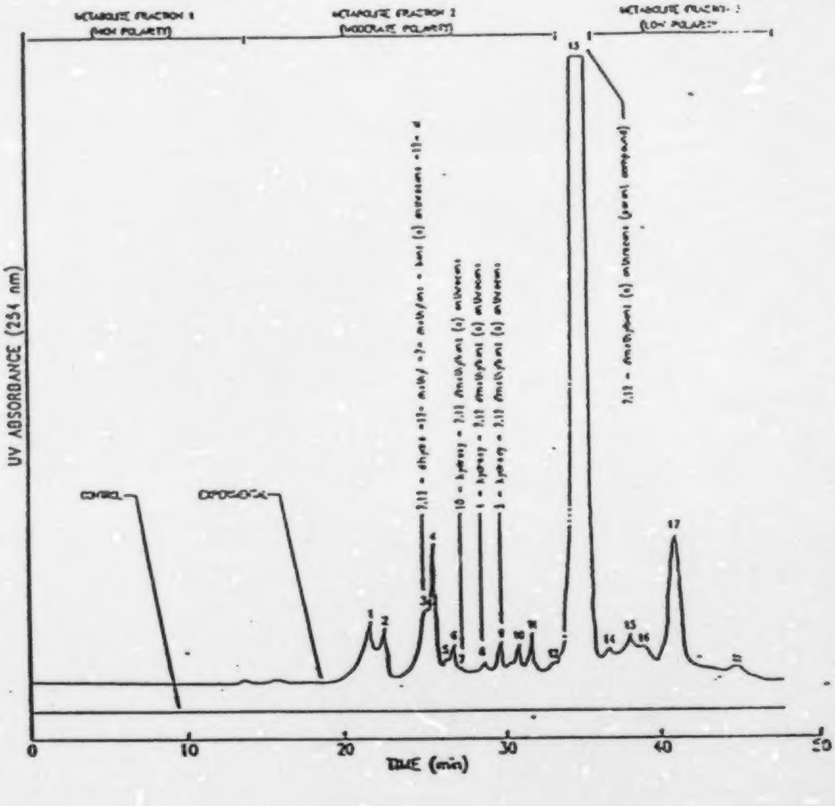


Figure 13. HPLC chromatogram of soil extract formed from 7,12-dimethylbenz(a)anthracene by McLaurin sandy loam soil (low pH).

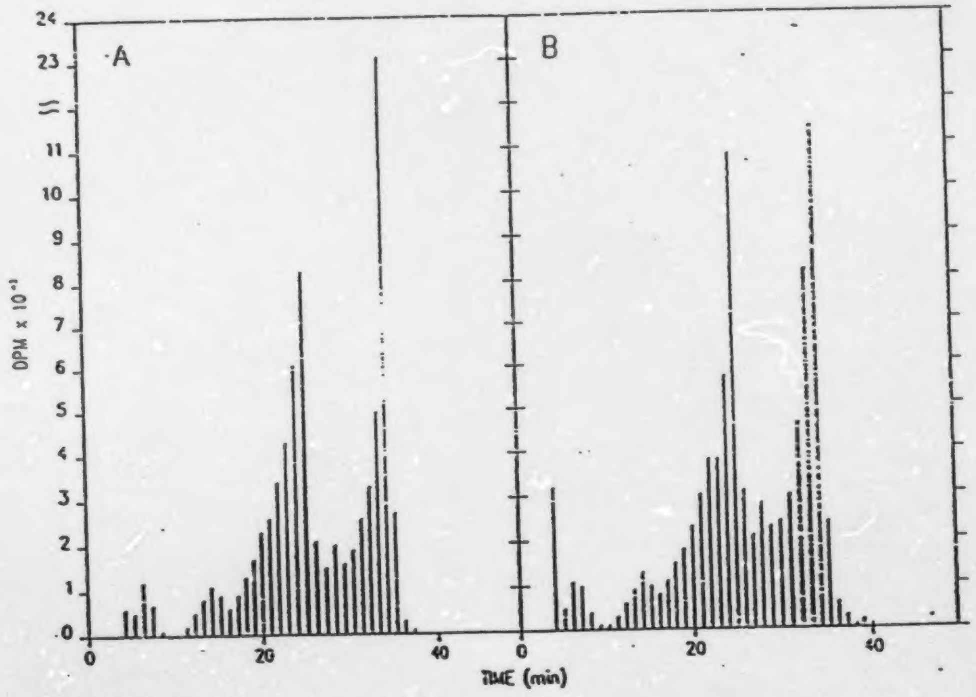


Figure 14. Elution profile of metabolites formed from (^{14}C) 7,12-dimethylbenz(a)anthracene by McLaurin sandy loam soil. (A) 14 days, (B) 28 days incubation time.

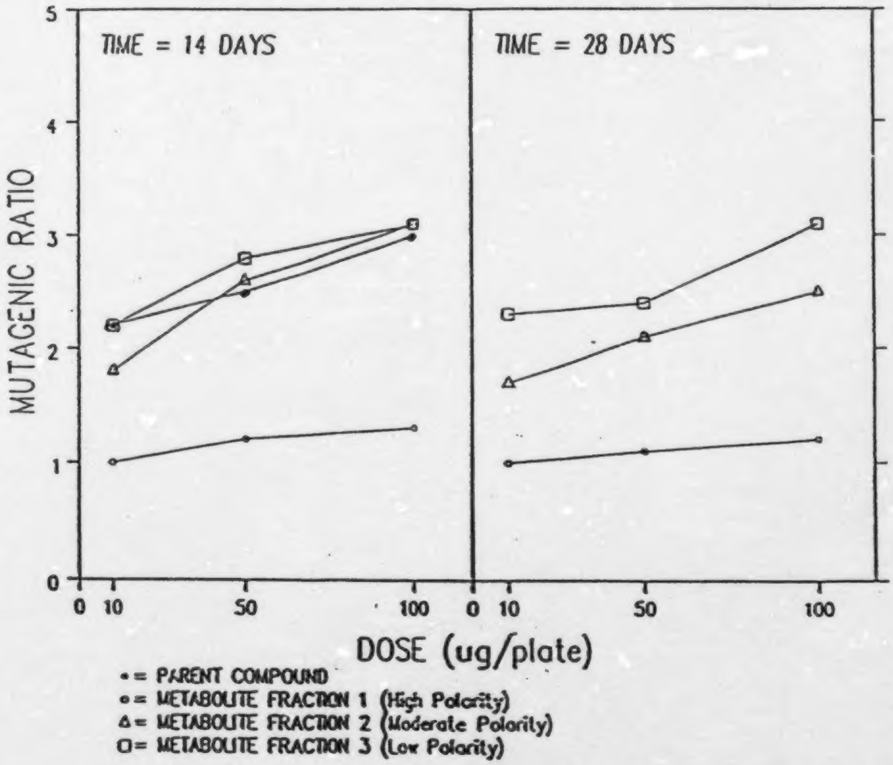


Figure 15. Mutagenicity of 7,12-dimethylbenz(a)anthracene metabolites from McLaurin sandy loam soil (low pH).

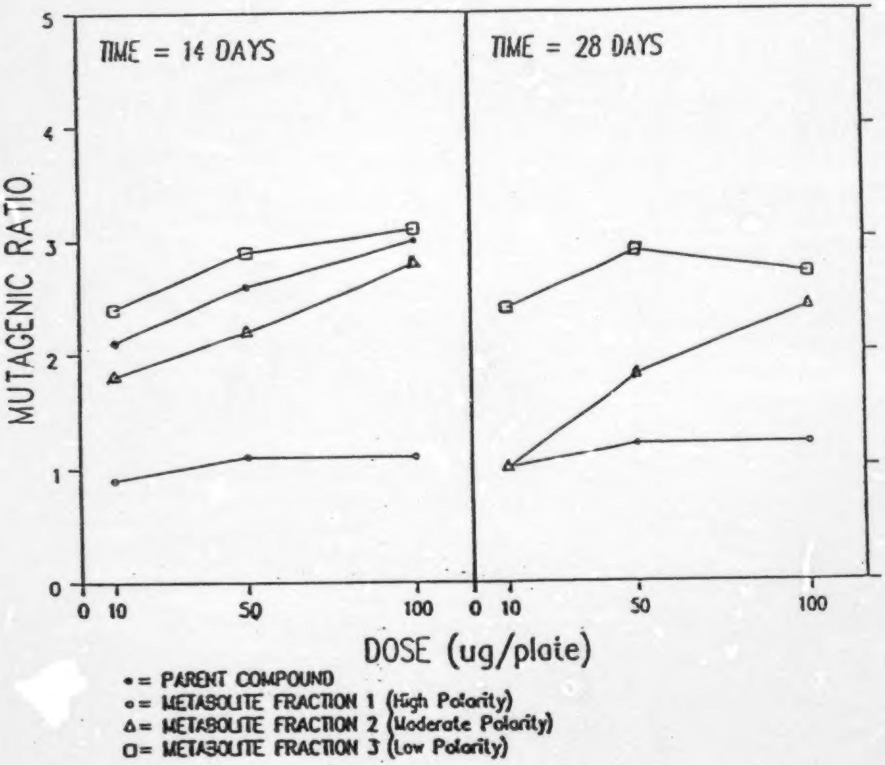


Figure 16. Mutagenicity of 7,12-dimethylbenz(a)anthracene metabolites from McLaurin sandy loam soil adjusted to neutral pH soil condition.

Compounds that were tentatively identified included 4-hydroxy-, 5-hydroxy-, and 10-hydroxy-DMBA and 7,12-dihydro-12-methyl-7-methylene-benz(a)anthracene-12-ol. High polarity transformation products of DMBA were not mutagenic for both low and neutral pH soil treatments. Moderate and low polarity metabolites, however, induced a positive response for both soil treatments. The mutagenic potential of these fractions decreased with increasing incubation time. Soil pH adjustment did not achieve a significant change in the microbial population and thus contributed to the similar mutagenic responses between the two pH soil treatments.

TABLE 35. EFFECT OF SOIL pH ON MICROBIAL POPULATIONS IN MCLAURIN SANDY LOAM SOIL

Soil pH	cfu/g soil	
	Bacteria	Fungi
4.8	1.1×10^5	5.3×10^4
7.5	2.5×10^6	4.0×10^3

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